Supreme Court, U.S.
FILED
JUL 30 1987
JOSEPH F. SPANIOL, JR.
CLERK

87-194
No. _____

In The

Supreme Court of the United States

October Term, 1987

TI-COATING, INCORPORATED,
Petitioner,

v.

SCHWARZKOPF DEVELOPMENT CORPORATION,
Respondent.

PETITION FOR A WRIT OF CERTIORARI TO THE UNITED STATES COURT OF APPEALS FOR THE SECOND CIRCUIT

- AND APPENDICES -

HARNESS, DICKEY & PIERCE
By: CHARLES H. BLAIR
Counsel of Record
1500 North Woodward Avenue
Birmingham, Michigan 48011
(313) 642-7000

Counsel for Petitioner

Interstate Brief & Record Co., Suite 731, David Whitney Building, Detroit, MI 48226
(313) 962-8745

QUESTION PRESENTED

WHETHER SUMMARY JUDGMENT AS TO THE MEANING OF A PATENT IN A CONTRACT IS PROPER WHEN THE LANGUAGE IS SUSCEPTIBLE OF TWO REASONABLE INTERPRETATIONS, AND WHEN DOING SO IMPLICITLY CREATES A CONFLICT WITH DECISIONS OF THE COURT OF APPEALS FOR THE FEDERAL CIRCUIT WHICH HAS EXCLUSIVE JURISDICTION OVER PATENT INFRINGEMENT SUITS.

RULE 21.1(a) STATEMENT

All parties to the proceeding are contained in the caption of the case in this Court.

RULE 28.1 STATEMENT

Ti-Coating has no parent company, subsidiaries which are not wholly owned, or affiliates.

TABLE OF CONTENTS

Page

QUESTION PRESENTED i

RULE 21.1(a) STATEMENT ii

RULE 28.1 STATEMENT ii

TABLE OF AUTHORITIES v

OPINIONS BELOW 1

JURISDICTION 2

STATEMENT OF THE CASE:

1. Introduction 2
2. Uncontested Facts 3
3. Evidence Presented By Ti-Coating To Support Its 'Narrow Interpretation' Of The Patents In The Contract 5
4. Evidence Presented By Schwarzkopf To Support Its 'Broad Interpretation' Of The Patents In The Contract 12
5. Decision Of The District Court And The Court Of Appeals For The Second Circuit 13

REASONS FOR GRANTING THE WRIT 17

CONCLUSION 21

APPENDICES:

Appendix A – ORDER of the Court of Appeals for the Second Circuit denying Petition for Rehearing *En Banc, Schwarzkopf Development Corporation* v. *Ti-Coating,* No. 86-7778, Slip. Op. (2nd Cir, April 29, 1987) A-1

Page

Appendix B – ORDER of the Court of Appeals for the Second Circuit, *Schwarzkopf Development Corporation* v. *Ti-Coating*, No. 86-7778, Slip. Op. (2nd Cir., March 2, 1987) B-1

Appendix C – ORDER of the Court of Appeals for the Federal Circuit transferring case to Court of Appeals for the Second Circuit, *Schwarzkopf Development Corporation* v. *Ti-Coating*, 800 F.2d 240 (Fed. Cir., August 20, 1986) C-1

Appendix D – ORDER of the District Court for the Southern District of New York denying Motion for Reconsideration, *Schwarzkopf Development Corporation* v. *Ti-Coating*, No. 83 Civ. 9042 (LBS) Slip Op. (S.D.N.Y., September 16, 1985) D-1

Appendix E – OPINION of the District Court for the Southern District of New York, *Schwarzkopf Development Corporation* v. *Ti-Coating*, No. 83 Civ. 9042 (LBS) Slip Op. (S.D.N.Y., July 9, 1985) . . E-1

Appendix F – LICENSE AGREEMENT between Schwarzkopf Development Corporation and Ti-Coating F-1

Appendix G – UNITED STATES PATENT No. 4,101,703 . . . . . G-1

Appendix H – UNITED STATES PATENT No. 4,162,338 . . . . . H-1

Page

Appendix I – DECISION from the Patent and Trademark Office Terminating the Reexamination of United States Patent No. 4,101,703 (February 27, 1985) . . I-1

Appendix J – AFFIDAVIT of Andrew E. Pierce (February 21, 1985) J-1

Appendix K – LETTER from Dr. John M. Blocher (November 13, 1984) K-1

Appendix L – SCHINTLMEISTER'S REPLY In Support Of Its Motion To Dismiss Ohlsson's Rule 231(a)(1) Motion, *Robert C. Post, et al,* v. *Fall J. O. W. Ohlsson, et al,* v. *Wilfried Schintlmeister,* Patent and Trademark Office Interference No. 99,391 (February 4, 1977) L-1

Appendix M – AMENDMENT to United States Serial No. 329,128 (August 20, 1974) . . M-1

TABLE OF AUTHORITIES

Cases:

Anderson v. *Liberty Lobby, Inc.*, 477 U.S. __, 91 L.Ed. 2d 202 (1986) 12, 14, 19

Bear Brand Hosiery Co. v. *Tights, Inc.*, 605 F.2d 723 (4th Cir. 1979) 20

Beighler v. *Kleppe*, 633 F.2d 531 (9th Cir. 1980) . . 14

Davis v. *Chevy Chase Financial Services*, 667 F.2d 160 (D.C. Cir. 1981) 20

Hettig & Co. v. *Union Mutual Life Insurance Co.*, 781 F.2d 1141 (5th Cir. 1986) 20

Page

Heyman v. *Commerce & Industry Insurance Co.*, 524 F.2d 1317 (2nd Cir. 1975) 17

Kangaroos U.S.A., Inc. v. *Caldor, Inc.*, 778 F.2d 1571 (Fed. Cir. 1985) 12

Locite Corp. v. *Ultraseal*, 781 F.2d 861 (Fed. Cir. 1985) 17, 20

McGill, Inc. v. *John Zinc Co.*, 736 F.2d 666 (Fed. Cir. 1984) 18

P.M. Palumbo v. *Don-Joy Co.*, 762 F.2d 969 (Fed. Cir. 1985) 17, 20

Rothenberg v. *Lincoln Farm Camp, Inc.*, 755 F.2d 1017 (2nd Cir. 1985) 17

Standard Oil Co. v. *American Cyanamid Co.*, 774 F.2d 448 (Fed. Cir. 1985) 9, 18

In re Yamamoto, 740 F.2d 1569 (Fed. Cir. 1984) . . 7

Statutes:

28 U.S.C. § 1254(1) 2
28 U.S.C. § 1295(a)(1) 21
28 U.S.C. § 1332(a) 5
35 U.S.C. § 302 6

Other:

H.R. No. 97-312, 97th Cong., 1st Sess. 20-23 (1981) 2, 21

H.R. Rep. No. 1307, pt. I, 96th Cong., 2nd Sess. 3, *reprinted in* 1980 U.S. Code Cong. & Ad. News. 6460, 6462 6

Federal Court Improvements Act of 1982, P.L. 97-164, 96 Stat. 25 (April 2, 1982) 21

No. _____

In The

Supreme Court of the United States

October Term, 1987

TI-COATING, INCORPORATED,

Petitioner,

v.

SCHWARZKOPF DEVELOPMENT CORPORATION,

Respondent.

PETITION FOR A WRIT OF CERTIORARI TO THE UNITED STATES COURT OF APPEALS FOR THE SECOND CIRCUIT

Petitioner Ti-Coating, Inc. respectfully prays that a writ of certiorari issue to review the judgment and Opinion of the United States Court of Appeals for the Second Circuit entered in this proceeding on March 2, 1987.

OPINIONS BELOW

The Opinion of the Court of Appeals for the Second Circuit is unreported and is reprinted in Appendix B. The Order of the Court of Appeals for the Second Circuit denying rehearing *en banc* is reprinted in Appendix A.

The Opinion of the District Court for the Southern District of New York is unreported and is reprinted in Appendix E. The District Court denied a motion for reconsideration, the decision of which is reprinted in Appendix D.

JURISDICTION

The original judgment of the Court of Appeals for the Second Circuit was entered on March 2, 1987. The subsequent Order of the Court of Appeals for the Second Circuit denying rehearing *en banc* was entered on April 29, 1987. The jurisdiction of this Court is invoked under 28 U.S.C. § 1254(1).

STATEMENT OF THE CASE

1. Introduction

The controversy which surrounds this Petition concerns the construction of a contract which granted limited rights to two patents. The Court of Appeals for the Second Circuit affirmed a decision on summary judgment, which was granted without an evidentiary hearing and despite substantial evidence presented in opposition, and which construed the patents in such a manner as to impose liability on the Petitioner. While the case involves the construction of patents, the appeal was heard by the Second Circuit since the suit was based on a contract.

Since 1982, the Court of Appeals for the Federal Circuit has had exclusive jurisdiction over appeals in patent infringement cases. The purpose of this grant of exclusive jurisdiction to the Federal Circuit was to provide uniformity in the application of the laws regarding patents. H.R. No. 97-312, 97th Cong., 1st Sess. 20-23 (1981). As will be described below, the decision on summary judgment as affirmed by the Second Circuit is implicitly in conflict with the decisions of the Federal Circuit regarding the rules used for construing patents. For this reason, and because of the basic errors in the appealed decision, it is submitted that this Petition

should be granted and that the decision of the Second Circuit in this case be reversed and this case remanded for determination consistent with the guidelines enunciated by the Federal Circuit regarding the construction of patents.

2. Uncontested Facts

The specific subject matter of the controversy relates to coatings applied to a wear surface (or substrate) of a tool to improve the wear characteristics. In December 1983, Ti-Coating, Inc. ("Ti-Coating") and Schwarzkopf Development Corporation ("Schwarzkopf") entered into a contract (or License Agreement) which is reprinted in Appendix F. The contract conveyed limited rights from Schwarzkopf to Ti-Coating to make, use and sell tools with multilayer wear coatings having miniscule layers of titanium carbide, titanium nitride and titanium carbonitride in certain specific combinations.[1] The coatings which are covered by this contract are specified by the claims of U.S. Patent Nos. 4,101,703 ("'703 patent") and 4,162,338 ("'338 patent") which are incorporated in the contract. The '703 patent is reprinted in Appendix G and the '338 patent is reprinted in Appendix H.

The controversy which gave rise to this Petition concerns whether a "particular coating" applied by Ti-Coating is covered by the terms of the contract. Unlike the coatings taught in the patents of the contract, "particular coating" applied by Ti-Coating included a protective, intervening barrier between the substrate (or work surface) of the tool and the wear coating. The "particular coating" had the following composition:

1. an intervening, protective barrier layer of titanium nitride applied directly to the substrate;

---

[1] The thicknesses of these miniscule layers ranges from .2-30 microns. A micron is about .00004 of an inch.

2. a multilayer wear coating applied to the barrier layer as follows:

    i. a titanium carbide layer directly on the intervening layer of titanium nitride;

    ii. a titanium carbonitride layer directly on the titanium carbide layer; and

    iii. a titanium nitride layer directly on the titanium carbonitride layer.

It is undisputed that the contract *does not* explicitly recite a coating having an intervening, barrier layer of titanium nitride between the substrate and the multilayer wear coating.[2] The controversy here is whether the patent and hence the contract is nevertheless broad enough to cover such a coating. For purposes of simplicity, the interpretation of the contract asserted by Schwarzkopf (*i.e.*, that the patents cover a coating with an intervening layer between the substrate and the multilayer wear coating) shall be referred to as the *'broad interpretation'*, while the interpretation of the contract asserted by Ti-Coating (*i.e.*, that the patents do not cover a coating with an intervening layer between the substrate and the multilayer wear coating) will be referred to as the *'narrow interpretation'*.

---

[2] For purposes of this Petition, the contract explicitly recites a multilayer coating as well as a method for applying the multilayer coating. This multilayer wear coating is embodied in Claim 15 of the '703 patent which does not explicitly recite the inclusion of an intervening layer between the substrate and the wear coating. Appendix G at G-20.

The method for applying the multilayer wear coating is embodied in Claim 21 of the '338 patent which also does not explicitly recite the formation of an intervening layer between the substrate and the multilayer wear coating. Appendix H at H-21.

3. Evidence Presented By Ti-Coating To Support Its 'Narrow Interpretation' Of The Patents In The Contract

After filing suit against Ti-Coating in the United States District Court for the Southern District of New York,[3] Schwarzkopf brought the dispute over the interpretation of the patents in the contract to the District Court on a motion for summary judgment. Ti-Coating firmly believed that the contract did not cover a coating having an intervening layer between the substrate and the multilayer wear coating. This was substantiated by the examples of the coatings taught in both the '703 and '338 patents.[4] The evidence which Ti-Coating presented to the District Court in opposition to summary judgment included the following:

i. a decision from the Patent and Trademark Office regarding a reexamination proceeding involving

---

[3] Federal jurisdiction of the District Court was based on diversity between the parties under 28 U.S.C. § 1332(a).

[4] The '703 and the '338 patents clearly disclose that the titanium carbide layer of the multilayer wear coating is to be in "direct contact" with the substrate. In this regard, Example IV of both patents states:

> Metallographic examination of the coating showed that depending on the chosen conditions, the coating comprises a 0.5 to 3 microns thick titanium carbide initial layer *in direct contact* with the cemented carbide element . . .
>
> Appendix G at G-17; Appendix H at 17.

A review of the other examples leads to the same conclusion. In Example I, the coatings "comprise a 0.5 to 3 microns thick initial layer of titanium carbonitride of high carbon content . . . *in contact with* the carburized cemented carbide substrate". Appendix G at G-13–G-14; Appendix H at H-13–H-14. In Example II, the "gas mixture reacts *at the surface* of the cemented carbide parts resulting in the deposition of a titanium carbonitride of high carbon content". Appendix G at G-14; Appendix H at H-14. In Example III, the patents state that "[t]he gas mixture reacts *at the surface* of the cemented carbide parts and titanium carbide is deposited". Appendix G at G-15; Appendix H at H-15.

the scope of certain claims of the '703 patent which the District Court later found *"almost identical"* [5] to one of the claims in issue (Appendix I);

ii. admissions made in the prosecution history by Schwarzkopf to the Patent and Trademark Office regarding the scope of the invention embodied in the '703 and '338 patents;

iii. the affidavit of Mr. Andrew E. Pierce, an expert in patent law with a background in chemistry (Appendix J); and

iv. a letter from Dr. John M. Blocher, Jr., former senior research scientist at Battelle Memorial Institute and an expert in the application of coatings by chemical vapor deposition in the manner described in the '703 and '338 patents (Appendix K).

In the reexamination proceeding,[6] a third party argued before the Patent and Trademark Office that certain claims of the '703 patent were unpatentable. The basis for this argument was that the claims were broad enough to cover a coating *having* an *intervening layer* between the substrate and the multilayer wear coating and that since this coating was previously known, *i.e.*, in the prior art, the claims were not patentable. Importantly, the coating upon which the third party based its argument is *almost identical* to the coating which is applied by Ti-Coating — both having an intervening

---

[5] Appendix E at E-7.

[6] Under 35 U.S.C. § 302, any person at any time may file a request for reexamination in the Patent and Trademark Office with respect to any claim of a United States patent. The purpose of the reexamination proceeding is to permit the Patent and Trademark Office to "review the efficacy of a patent, subsequent to issuance, on the basis of new information about pre-existing technology which may have escaped review at the time of the initial examination of the patent application". H.R. Rep. No. 1307, pt. I, 96th Cong., 2d Sess. 3, *reprinted in* 1980 U.S. Code Cong. & Ad. News. 6460, 6462.

layer between the substrate and the multilayer wear coating.

The Patent and Trademark Office rejected the assertion that these claims were broad enough to cover coatings such as the one applied by Ti-Coating. In determining that Claims 3-6 of the '703 patent were not broad enough to cover a coating with an intervening layer, the Patent and Trademark Office specifically found that the first layer of the wear coating, the miniscule layer of titanium carbide, had to be applied *directly to* the substrate or wear surface of the tool. In this regard, the Patent and Trademark Office held:

> [The requestor] [a]lleges that using the rationale set forth in the decision of *In re Yamamoto*, 740 F.2d 1569 (Fed. Cir. 1984), claims 3-6 can be interpreted to include an intervening layer between the cemented carbide substrate and the titanium carbide layer. Claim 3 calls for an article comprising said substrate and a composite coating on at least one surface of said substrate. *If in fact there is an intervening layer the titanium carbide would not be on the substrate but on the intervening layer.* Claim 6 calls for a wear surface comprised of a hard metal or sintered carbide, a coating of titanium carbide covering said wear surface and a coating of titanium article covering said coating of titanium carbide. *This claim calls for the titanium to cover the wear surface — not any other surface or layer.*
>
> * * *
>
> The prior art was considered in the context of the claims [of the '703 patent] *requiring* the titanium carbide layer to be in *contact* with the wear surface and said claims have been found patentable over the prior art of record.
>
> Appendix I at I-1 – I-2 (emphasis added).

Accordingly, the interpretation of Claims 3-6 of the '703 patent by the Patent and Trademark Office was *identical* to the 'narrow interpretation' of the patents asserted by Ti-Coating: that the wear coating had to be directly on the substrate. While the reexamination proceeding concerned Claims 3-6 of the '703 patent, the District Court held that Claim 3 was "almost identical" to Claim 15 which Schwarzkopf asserted made Ti-Coating liable under the contract, *i.e.*, both require "a composite coating *on* at least one surface of said substrate". Appendix E at E-7.

The District Court also had documents from the prosecution history of the patents which had been submitted by Schwarzkopf to the Patent and Trademark Office in which Schwarzkopf admitted that the invention embodied in the '703 and '338 patents did not cover a coating with an intervening layer. For example, Schwarzkopf argued during a priority contest in the Patent and Trademark Office that its invention was an improvement over the existing coatings which *included* an intervening layer between the substrate and the wear coating. In this regard, Schwarzkopf stated:

> None of the references describe a substrate coated with titanium carbide with an overlayer thereon of titanium nitride. To the extent that these references disclose use of more than one coating layer, *they teach the necessity of having the nitride in contact with the base metal*. See, for example, British Patent No. 735,297; British Patent No. 762,931; German Patent No. 1,954,366 and U.S. Patent No. 3,656,995. Indeed, the latter patent explains the art felt need for initially forming a *protective* [*titanium*] *nitride barrier layer on the substrate before any further activity*.
>
> Appendix L at L-4 (emphasis added).

The prosecution history further shows that Schwarzkopf repeated these admissions to the Patent and Trademark Office on various other occasions. Appendix M at M-6, M-8.

Thus the prosecution history shows that Schwarzkopf repeatedly distinguished the application which matured into the '703 and '338 patents from that which was already known on the basis that the coating claimed in the application did *not* have an intervening layer. It is well established that such admissions are binding in subsequent proceedings. *Standard Oil Co.* v. *American Cyanamid Co.*, 774 F.2d 448 (Fed. Cir. 1985) ("[T]he prosecution history (or file wrapper) limits the interpretation of claims so as to exclude any interpretation that may have been disclaimed or disavowed during prosecution in order to obtain claim allowance", *Id.* at 452). Clearly even this limited portion of the prosecution history supports the finding by the Patent and Trademark Office in the reexamination proceeding that the patents do not cover a coating with an intervening layer. But this finding was rejected without reference to its correctness and without consideration of the prosecution history upon which this finding was based.

Ti-Coating also presented to the District Court the Affidavit of Andrew E. Pierce — an expert in patent law with a background in chemistry. The Affidavit of Mr. Pierce is reprinted in Appendix J. To permit Mr. Pierce to ascertain the scope of the '703 and the '338 patents and therefore the liability of Ti-Coating under the contract, Mr. Pierce reviewed the following documents included within the prosecution history of the patents:

i. The '703 patent and the documents relating to its issuance;

ii. the patent applications relating to the '703 patent, and the documents filed in the Patent and Trade-

mark Office relating thereto including the cited references;

iii. the '338 patent and documents relating to its issue;

iv. the patent applications which were related to the '338 patent patent, the documents filed in the Patent and Trademark Office relating thereto including the cited references;

v. documents relating to patent interference No. 99,391 which involved the patent application which ultimately led to the '703 and '338 patents.

After considering these documents, Mr. Pierce concluded that the claims in *both* the '338 and '703 patents *required* that the wear coating be *directly on* the surface of the substrate rather than on an intervening layer. Appendix J at J-6–J-8. Accordingly, the Affidavit of Mr. Pierce also supports the 'narrow interpretation' of the patents found by the Patent and Trademark Office, *i.e.*, that the patents do not cover a coating having an intervening layer between the substrate and the multilayer wear coating.

Also submitted to the District Court was a letter by Dr. John Blocher, Jr. which is reprinted in Appendix K. Dr. Blocher, a former senior research scientist at Battelle Memorial Institute, is an expert on the formation of coatings by chemical vapor deposition such as those covered by the '338 and the '703 patents. Dr. Blocher also concluded that proper interpretation of the patents requires that the first layer of the wear coating, the miniscule layer of titanium carbide, be *directly* on the substrate. As Dr. Blocher stated:

> It will be noted that most of the claims clearly specify that the [titanium] carbide coating be

> applied directly to the metal carbide substrate, this to be overcoated with the nitride, with or without an intermediate carbonitride. I am convinced that Schintlmeister either did not anticipate the advantage of using a preliminary nitride coating, or that he avoided its mention for some unexplained reason. Otherwise, he would have included a claim that spelled it out.
>
> * * *
>
> It is to be noted that all of the examples have a carbide coating adjacent the substrate, and that at no place in the text is the possibility of an intervening coating suggested or allowed.
>
> Appendix K at K-5.

The statements of Dr. Blocher therefore also support the 'narrow interpretation' of the patents found by the Patent and Trademark Office and as asserted by Ti-Coating.

In summary, the decision of the Patent and Trademark Office in the reexamination proceeding supported the 'narrow interpretation' of the contract patents asserted by Ti-Coating — that the contract does not cover a coating with an intervening layer between the substrate and the wear coating. The decision of the Patent and Trademark Office was supported by the prosecution history and was independently corroborated by the Affidavit of Mr. Pierce and the letter of Dr. Blocher, which were presented to the District Court *before* the decision from the Patent and Trademark Office was issued.[7] Since this appeal is from the grant of summary judgment against Ti-Coating, this evidence must

---

[7] The Affidavit of Mr. Pierce and the letter of Dr. Blocher were filed with the District Court on February 25, 1985, while the decision from the Patent and Trademark Office issued on February 27, 1985.

be considered true. *Anderson* v. *Liberty Lobby, Inc.*, 477 U.S. __, 91 L.Ed. 2d 202 (1986) ("[t]he evidence of the nonmovant is to be believed, and all justifiable inferences are to be drawn in his favor", *Id.* at 216); *Kangaroos U.S.A., Inc.* v. *Caldor, Inc.*, 778 F.2d 1571 (Fed. Cir. 1985) ("the district court must view the evidence in the light most favorable to the party against whom the summary judgment is directed and reasonable inferences of fact must be drawn in vavor of the non-movant", *Id.* at 1573).

4. Evidence Presented By Schwarzkopf To Support Its 'Broad Interpretation' Of The Patents In The Contract

No affidavits or any other form of evidence was submitted by Schwarzkopf to support its 'broad interpretation' of the patents. Rather, Schwarzkopf relied entirely on its own self-serving statements. Importantly, Schwarzkopf presented no evidence which showed that the decision of the Patent and Trademark Office was flawed, it presented no evidence rebutting the statements it made to the Patent and Trademark Office advocating a 'narrow construction' to obtain the patents, nor did it present evidence to rebut the findings set forth in the Affidavit of Mr. Pierce or in the letter of Dr. Blocher. Schwarzkopf only challenged the 'narrow interpretation' of the patents asserted by Ti-Coating by attacking the credibility of the Affidavit of Mr. Pierce and the letter of Dr. Blocher. However, a challenge to the credibility of evidence submitted by the nonmovant is irrelevant when an issue is being resolved on summary judgment. *Anderson* v. *Liberty Lobby, Inc.*, 477 U.S. __, 91 L.Ed. 2d 202 (1986) ("[c]redibility determinations, weighing of the evidence, and the drawing of legitimate inferences from the facts are jury functions, not those of a judge", *Id.* at 216).

5. Decision Of The District Court And The Court Of Appeals For The Second Circuit

Rather than recognizing that a triable issue of fact existed as two reasonable interpretations of the patents in the contract were possible, the District Court adopted the 'broad interpretation' of the patents asserted by Schwarzkopf. This despite the fact that no evidence was presented by Schwarzkopf to rebut the interpretation adopted by the Patent and Trademark Office and independently supported by the prosecution history of the patents, the Affidavit of Mr. Pierce and the letter of Dr. Blocher.

The District Court without reference to the prosecution history dismissed the decision of the Patent and Trademark Office simply noting that the District Court was not bound by the rulings from the Patent and Trademark Office. In this regard, the decision of the District Court, as adopted by the Second Circuit, stated.

> The P.T.O. decision of February 27, 1985, denying a third party's petition for reexamination of the plaintiff's patent, interpreted claims 3-6 of patent '703. The language of these claims is very similar to the language of claims 15-17 of '703, the claims at issue here. The P.T.O. interpreted the language of patent claims 3-6 as not contemplating the addition of an intermediate layer between the substrate of the tool and the plaintiff's patented three-layer coating. While we acknowledge that the language of claims 3-6 is almost identical to the language of claims 15-17, *this Court will not follow the P.T.O.'s interpretation* for the following reasons.
>
> As an initial matter, we note that the P.T.O. does not have an estoppel or other legally binding

> effect on this Court especially where, as here, the statements of the P.T.O. are made in a determination upholding a decision declining to reexamine an already issued patent, in a proceeding in which the patentee was not a party and, under P.T.O. rules, could not participate. A court, in evaluating the validity of a patent, must give "due respect" to P.T.O. decisions but is not bound thereby.
>
> Appendix E at E-7–E-8 (emphasis added).

The District Court therefore dismissed the findings of the Patent and Trademark Office even though, *on summary judgment*, these findings are to be believed and all justifiable inferences therefrom are to be drawn in favor of Ti-Coating. *Anderson* v. *Liberty Lobby, Inc.*, 477 U.S. __, 91 L.Ed. 2d 202 (1986) ("[t]he evidence of the nonmovant is to be believed, and all justifiable inferences are to be drawn in his favor", *Id.* at 216).

The District Court, again without reference to the prosecution history, dismissed the Affidavit of Mr. Pierce for two reasons. First, the District Court stated that the Affidavit of Mr. Pierce was faulty as it relied on the unsworn statements concerning the composition of the coating applied by Ti-Coating. Appendix E at E-5. Besides the fact that the composition of the coating applied by Ti-Coating was *never* disputed by the parties, Fed. R. Evid. 703 explicitly permits an expert to rely on unsworn statements when used in forming the expert's opinion. See also *Beighler* v. *Kleppe*, 633 F.2d 531 (9th Cir. 1980) (Court held admissible under Fed. R. Evid. 703 an affidavit of an expert made in opposition to summary judgment under Fed. R. Civ. P. 56(e) which was based in part on hearsay statements of the party opposing the motion).

Second, the District Court stated that the statements made in the Affidavit of Mr. Pierce went to "functional equivalence, which is irrelevant to determining literal infringement". Appendix E at E-5. Yet nowhere in the Affidavit of Mr. Pierce did the affiant limit the scope of his findings to functional equivalence.[8]

With respect to the letter of Dr. Blocher, the District Court considered only a statement made by Dr. Blocher when he speculated that Claim 15 of the '703 patent could be read to include an intervening layer. In this regard, the District Court stated:

> Indeed, the defendant's own expert, Dr. John Blocher, Jr. in a letter to Ti-Coating President Zichichi, acknowledged that the word "include" as it appears in '703 claim 15 might result in literal infringement even where there is an intermediate coating between the substrate and the other layers.
>
> Appendix E at E-4.

---

[8] Indeed, Mr. Pierce explicitly concluded that the broadest claims of either the '703 patent or the '338 patent were not sufficiently broad to cover the coating applied by Ti-Coating:

> (b) The broadest claims of the '703 patent patent, namely, claims 1, 3, 6, 8, 15, 16, 17, and 19 are not of sufficient scope to encompass the coated metal carbide substrate articles produced by the process of Ti-Coating, Inc.;
>
> * * *
>
> (d) The broadest claims of the '338 patent, namely, claims 1, 2, 3, 20, and 16, are not of sufficient scope to encompass the process of producing sintered carbide substrates coated with the wear-resistant layers of Ti-Coating, Inc.
>
> Appendix J at J-7 – J-8.

Neither of these conclusions were qualified by any requirement of functional equivalence.

However, the District Court ignored the statements made by Dr. Blocher in which he concluded that if Claim 15 were so interpreted, Schwarzkopf would have "lucked out" as the patentee obviously intended *not* to claim a coating with an intervening layer. In this regard, Dr. Blocher stated:

> If that is ruled to be the valid interpretation, I would conclude that Schintelmeister [*sic*] "lucked out" on that one, because his intent is obviously not to clearly claim such an intermediate coating. It is to be noted that all of the examples have a carbide coating adjacent the substrate, and that at no place in the text is the possibility of an intervening coating suggested or allowed.
>
> Appendix K at K-5.

Finally, the District Court made no finding rebutting the admissions by Schwarzkopf to the Patent and Trademark Office in which Schwarzkopf represented that the application which matured into the '703 and '338 patents did not cover a coating with an intervening layer. These admissions were presumably ignored.

The decision of the District Court was affirmed on appeal by the Court of Appeals for the Second Circuit. In addressing the merits of the case, the Second Circuit merely stated: "[f]or substantially the reasons set forth in Judge Sand's opinion, the judgment of the District Court is affirmed". Appendix B at B-2.

REASONS FOR GRANTING THE WRIT

When the meaning of a claim in a patent is in dispute and extrinsic evidence is necessary to explain the language of the claim, summary judgment is improper. In this regard, the Court of Appeals for the Federal Circuit has held:

> But when the meaning of a term in the claim is disputed and extrinsic evidence is necessary to explain that term, an underlying factual question arises, and construction of the claim should be left to the trier or jury under appropriate instructions.
>
> *P.M. Palumbo* v. *Don-Joy Co.*, 762 F.2d 969, 974 (Fed. Cir. 1985).

Prior to its decision in this case, this was essentially the same rule that was applied by the Court of Appeals for the Second Circuit with respect to contracts. *Heyman* v. *Commerce & Industry Insurance Co.*, 524 F.2d 1317 (2nd Cir. 1975) ("[w]here contractual language is susceptible of at least two fairly reasonable interpretations, this presents a triable issue of fact and summary judgment would be improper," *Id.* at 1320). See also *Rothenberg* v. *Lincoln Farm Camp, Inc.*, 755 F.2d 1017 (2nd Cir. 1985).

Since the Court of Appeals for the Federal Circuit has exclusive jurisdiction over patent infringement suits, the rules of the Federal Circuit should be used to construe patents. Under the rules of the Federal Circuit, patents must be viewed in light of the prosecution history as a *preliminary* step to a *proper interpretation*. *Loctite Corp.* v. *Ultraseal*, 781 F.2d 861 (Fed. Cir. 1985) ("[i]nterpreting claims in view of the prosecution history applies as a preliminary step in determining literal infringement", *Id.* at 870). In this regard:

> The prosecution history (or file wrapper) limits the interpretation of claims so as to exclude any interpretation that may have been disclaimed or disavowed during prosecution in order to obtain claim allowance.
>
> *Standard Oil Co.* v. *American Cyanamid Co.*, 774 F.2d 448, 452 (Fed. Cir. 1985).

The prosecution history should be used not only as a claim construction tool during an infringement determination but also in an estoppel context. *McGill, Inc.* v. *John Zinc Co.*, 736 F.2d 666 (Fed. Cir. 1984) ("[p]rosecution history may be used not only in the estoppel context but also as a claim construction tool", *Id.* at 673). The prosecution history must therefore be assessed in properly interpreting claim language.

Though required to do so under the law developed by the Federal Circuit, the Second Circuit completely ignored the prosecution history of the patents. As discussed above, the prosecution history of the patents shows that Schwarzkopf consistently advocated a narrow construction to obtain the patents. The only decision regarding the scope of the patents in which the prosecution history was considered, therefore, was that rendered by the Patent and Trademark Office during the reexamination proceeding. This decision specifically found that the claims do not cover a coating with an intervening layer:

> The prior art was considered in the context of the claims *requiring* the titanium carbide layer [the first layer of the multilayer wear coating] to be in *contact* with the wear surface and said claims have been found patentable over the prior art.
>
> Appendix I at I-2.

Yet this finding by the Patent and Trademark Office, an agency which is charged with the responsibility of examining and determining the patentability of inventions, was rejected by the District Court and the Court of Appeals in affirmance without a single reference to the prosecution history to show the error of that finding!

In addition, the decision of the Patent and Trademark Office was independently corroborated by the Affidavit of Mr. Pierce in which Mr. Pierce, *after examining the prosecution history*, concluded that the '703 and '338 patents *required* the wear coating layer to be directly on the substrate and not on an intervening layer. Appendix J at J-6–J-8. The decision of the Patent and Trademark Office was further independently corroborated by the letter of Dr. Blocher, in which Dr. Blocher concluded that the patentee either did not anticipate the advantage of using an initial intervening layer or avoided its mention because the patentee's intent was obviously *not* to claim such an intermediate coating. Appendix K at K-5. Since the appeal is from the grant of summary judgment against Ti-Coating, the evidence presented by Ti-Coating *must* be considered true. *Anderson* v. *Liberty Lobby, Inc.*, 477 U.S. __, 91 L.Ed. 2d 202 (1986) ("[t]he evidence of the nonmovant is to be believed, and all justifiable inferences are to be drawn in his favor", *Id.* at 216).

Accordingly, there can be no doubt that the 'narrow interpretation' of the claims asserted by Ti-Coating is reasonable. Rather than deny summary judgment, the District Court and the Second Circuit in affirmance granted summary judgment despite the fact that two reasonable interpretations of the claims existed. The precedent thus created by the Second Circuit would permit summary judgment in a lawsuit involving a contract incorporating a patent without the necessary reference to the prosecution history of the patent. This conflicts

with the law of the Federal Circuit in which the prosecution history of the patents must always be considered when determining literal infringement. *Loctite Corp* v. *Ultraseal*, 781 F.2d 861 (Fed. Cir. 1985) ("[i]nterpreting claims in view of the prosecution history applies as a preliminary step in determining literal infringement", *Id.* at 870).

In addition, the precedent created by the Second Circuit in this case would also permit summary judgment in a lawsuit involving a contract incorporating a patent notwithstanding the fact that two reasonable but significantly different interpretations of the claims may be possible. This conflicts with the law of the Federal Circuit which holds that summary judgment is improper when the meaning of a claim is disputed and extrinsic evidence is necessary to explain the claims. *P. M. Palumbo* v. *Don-Joy Co.*, 762 F.2d 969 (Fed. Cir. 1985) ("[b]ut when the meaning of a term in a claim is disputed and extrinsic evidence is necessary to explain that term, then *factual question arises* and construction of the claim should be left to the trier or jury under appropriate instruction", *Id.* at 974). See also *Bear Brand Hosiery Co.* v. *Tights, Inc.*, 605 F.2d 723 (4th Cir. 1979) ("[o]nly an unambiguous writing justified summary judgment, and no writing is unambiguous if 'susceptible of two reasonable interpretations'" *Id.* at 726); *Hettig & Co.* v. *Union Mutual Life Insurance Co.*, 781 F.2d 1141 (5th Cir. 1986) ("[b]ecause the provisions are susceptible of either of two opposing interpretations, we find them ambiguous, and reverse and remand", *Id.* at 1142); *Davis* v. *Chevy Chase Financial Services*, 667 F.2d 160 (D.C. Cir. 1981) ("[w]here contractual language is susceptible of at least two fairly reasonable interpretations, this presents a triable issue of fact, and summary judgment would be improper", *Id.* at 169).

The need for resolution of this conflict cannot be understated. Since the passage of the Federal Court Improvements Act of 1982, P.L. 97-164, 96 Stat. 25 (April 2, 1982), lawsuits involving infringement of patents are appealed to the Court of Appeals for the Federal Circuit, while lawsuits involving contracts incorporating patents are appealed to the courts of appeals for the regional circuits. 28 U.S.C. § 1295(a)(1). The legislative intent behind the Federal Court Improvements Act was to provide uniformity in the decisions in the laws relating to patents. H.R. No. 97-312, 97th Cong., 1st Sess. 20-23 (1981). The dichotomy created by the Court of Appeals for the Second Circuit in this case frustrates the intent behind the Federal Court Improvements Act. The Second Circuit now permits summary judgment without reference to the prosecution history which would show that two reasonable interpretations of a particular patent incorporated within a contract exist. In contrast, the Federal Circuit would prohibit summary judgment when the same patent was involved in an infringement suit.

CONCLUSION

When the prosecution history and the other evidence discussed above is viewed in a light most favorable to Ti-Coating, the contract is reasonably susceptible of a narrow construction in which the patents do not cover the coating applied by Ti-Coating. While Schwarzkopf relies on a broader construction of the patents, this construction is in conflict with the myriad of facts submitted by Ti-Coating. Summary judgment is therefore improper under the guidelines set forth by the Court of Appeals for the Federal Circuit in patent infringement cases. It is respectfully urged that the Supreme Court direct the regional circuits to follow the decisions of the Court of

Appeals for the Federal Circuit in construing patents in contract and other cases. Accordingly, the grant of this Petition for Writ of Certiorari is most respectfully requested.

Respectfully submitted,

HARNESS, DICKEY & PIERCE
By: CHARLES H. BLAIR
Counsel of Record
1500 North Woodward Avenue
Birmingham, Michigan 48011
(313) 642-7000

Counsel for Petitioner

Dated: July 24, 1987

APPENDICES TO PETITION FOR CERTIORARI

• • •

APPENDIX A

ORDER DENYING REHEARING *EN BANC*

(United States Court of Appeals for the Second Circuit)

(Filed April 29, 1987)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff-Appellee, v. TI-COATING, INC., Defendant-Appellant – No. 86-7778)

At a stated Term of the United States Court of Appeals, in and for the Second Circuit, held at the United States Courthouse in the City of New York, on the twenty-ninth day of April, one thousand nine hundred and eighty-seven.

A petition for rehearing containing a suggestion that the action be reheard in banc having been filed herein by counsel for the defendant-appellant Ti-Coating, Inc.,

Upon consideration by the panel that heard the appeal, it is ORDERED that said petition for rehearing is DENIED.

It is further noted that the suggestion for rehearing in banc has been transmitted to the judges of the court in regular active service and to any other judge that heard the appeal and that no such judge has requested that a vote be taken thereon.

/s/ Elaine B. Goldsmith,
Clerk

APPENDIX B

ORDER

(United States Court of Appeals for the Second Circuit)

(Filed March 2, 1987)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff-Appellee, v. TI-COATING, INC., Defendant-Appellant – 86-7778)

At a stated Term of the United States Court of Appeals for the Second Circuit, held at the United States Courthouse in the City of New York, on the second day of March, one thousand nine hundred and eighty-seven.

Present: HONORABLE JON O. NEWMAN, HONORABLE RICHARD J. CARDAMONE, HONORABLE RALPH K. WINTER, Circuit Judges.

Ti-Coating, Inc. appeals from a judgment of the District Court for the Southern District of New York (Leonard B. Sand, Judge) granting summary judgment in favor of plaintiff-appellee Schwarzkopf Development Corporation in a suit seeking royalties under a patent license. Ti-Coating had defended the claim on the ground that its product does not infringe the licensed patent. The patent concerns a multi-layered wear coating for application on a substrate. Ti-Coating contends that it does not infringe the patent because it applies an initial layer of titanium nitride on the substrate before application of the multi-layered composition described in plaintiff's patent. This contention was carefully analyzed by Judge Sand and rejected on the basis of undisputed facts and applicable law.

For substantially the reasons set forth in Judge Sand's opinion, the judgment of the District Court is affirmed.

/s/ Jon O. Newman
/s/ Richard J. Cardamone
/s/ Ralph K. Winter
Circuit Judges.

N. B. Since this statement does not constitute a formal opinion of this court and is not uniformly available to all parties, it shall not be reported, cited or otherwise used in unrelated cases before this or any other court.

APPENDIX C

ORDER

(United States Court of Appeals for the Federal Circuit)

(Dated August 20, 1986)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff-Appellee, v. TI-COATING, INC., Defendant-Appellant – Appeal No. 86-788; ON MOTION TO DISMISS OR TRANSFER)

Joseph R. Papp, Harness, Dickey and Pierce, of Birmingham, Michigan, represented the appellant.
David H. Pfeffer, Morgan, Finnegan, Pine, Foley and Lee, of New York, New York, represented the appellee.
Appealed from: United States District Court for the Southern District of New York; Judge Sand.

Before NEWMAN, BISSELL, and ARCHER, *Circuit Judges*.

NEWMAN, *Circuit Judge*.

Appellee Schwarzkopf Development Corporation (SDC) moves to dismiss or transfer this appeal under 28 U.S.C. § 1631 for lack of appellate jurisdiction in the Federal Circuit.

The complaint raised claims in contract and (as amended) contracted-related tort. The action was initiated by SDC in state court and, before Ti-Coating's answer was filed, was transferred to federal court on diversity grounds. The answer filed in federal court contained patent-related defenses and a counterclaim that included patent counts. The counterclaim was dismissed in its entirety, without objection by the counterclaimant, before the filing of an answer thereto. On this procedural history, the motion to transfer is granted.

BACKGROUND

Portions of the factual and procedural background of this litigation are pertinent to our decision on jurisdiction. SDC is the owner of U.S. Patent No. 4,101,703 ("the '703 patent") and U.S. Patent No. 4,162,338 ("the '338 patent"), both directed to "Coated Cemented Carbide Elements". In November or December 1982 SDC and Ti-Coating entered into a written agreement, effective as of June 1, 1982, wherein SDC granted Ti-Coating a nonexclusive license to practice the inventions claimed in the SDC patents. The agreement released Ti-Coating from liability for past infringement and provided for the payment of royalties for operations after June 1, 1982.

The patented inventions relate to a multi-layered titanium-containing coating applied to cutting tools to increase their durability. Before November 1982 Ti-Coating had applied the patented coating directly to the surface of its tools. In November 1982 Ti-Coating assertedly changed its product by interposing an additional layer, ½ to 1 micron in thickness, of titanium nitride between the multi-layered coating and the tool surface. Ti-Coating paid no royalties for the periods before and after this change.

On November 14, 1983 SDC filed suit in New York state court for royalties due under the license agreement. Ti-Coating, a Michigan corporation, moved on December 13, 1983 to remove the suit pursuant to 28 U.S.C. § 1441 to the U.S. District Court for the Southern District of New York, alleging diversity jurisdiction under 28 U.S.C. § 1332. That motion was granted.

The action in the Southern District of New York was stayed, pending resolution of an earlier-filed action by Ti-Coating in Michigan arising out of the same transaction. The action had been filed in Michigan state court

for reformation of the license agreement, and had been removed, because of diversity, to federal court in Michigan on SDC's motion. Although Ti-Coating's Michigan complaint was subsequently amended in the federal court to include counts for declaratory judgment that the '703 and '338 patents were invalid, unenforceable, and not infringed, these and all other aspects of the Michigan action were dismissed. Ti-Coating's appeal to the Sixth Circuit was dismissed for lack of prosecution.

On June 12, 1984, after the dismissal of Ti-Coating's Michigan action, the Southern District of New York reactivated this action. On July 23, 1984 Ti-Coating filed an answer and counterclaim. Ti-Coating admitted that it had at one time practiced the patented inventions but denied doing so after November 1, 1982. Ti-Coating's answer raised nine defenses, including the defenses of patent invalidity, unenforceability, misuse, and noninfringement. Ti-Coating's counterclaim contained five counts: Count I, for which jurisdiction was based on 28 U.S.C. §§ 1338, 2201, and 2202, sought a declaratory judgment that the licensed patents were invalid, unenforceable, and not infringed; Count II alleged Sherman and Clayton Act violations; Count III, based on 28 U.S.C. §§ 1338 and 2202, sought a declaratory judgment that SDC had misused the licensed patents which were therefore unenforceable; Count IV asked for rescission of the license agreement; and Count V asked for its reformation.

All five counts of the counterclaim were dismissed on SDC's motion, without opposition by Ti-Coating. On August 31, 1984, SDC had moved under Fed. R. Civ. P. 12(b)(1) to dismiss Counts I and III for lack of justiciable controversy under the Declaratory Judgment Act, and as *res judicata* because the same counts had been dismissed in the Michigan action on the same grounds. SDC moved

under Fed. R. Civ. P. 12(b)(6) to dismiss Counts II and V for failure to state a claim for which relief could be granted, and as *res judicata*. Ti-Coating filed no opposition, and on October 4, 1984 the district court dismissed Counts I, II, III, and V of the counterclaim.

SDC filed a separate motion to dismiss Count IV and for partial summary judgment as to Ti-Coating's liability for royalties accrued between June 1, 1982 and November 1, 1982. Ti-Coating did not oppose, and this motion was granted on October 9, 1984.

SDC's motion to dismiss counterclaim Counts I, II, III, and V included a request for costs and attorney fees incident to the motion, on the ground that "there was no reasonable basis for the belief that these counts could properly be interposed in this action". Ti-Coating opposed this request, and on December 3, 1984 the district court denied attorney fees, stating that SDC had not clearly demonstrated that Ti-Coating's counterclaim was "entirely without color and . . . asserted wantonly, for purposes of harassment or delay, or for other improper reasons".

On December 10, 1984 SDC moved for a second partial summary judgment of royalty liability, based on Ti-Coating's products sold between November 1, 1982 and September 30, 1983. On January 29, 1985 the court conditionally granted this motion, observing that Ti-Coating had offered no evidentiary support for its defense that it did not infringe SDC's patents. The court also granted SDC leave to file an amended complaint introducing a count for fraudulent inducement to enter into the license agreement.

On May 30, 1985 SDC moved for partial summary judgment for damages based on the conditional holding of January 29, 1985. SDC countered Ti-Coating's defense

of patent invalidity on the basis that Ti-Coating "had failed to give prior notice of invalidity to Plaintiff and hence the defense of invalidity could not be raised for royalties due prior to the time of notice", which was October 30, 1983.

On July 9, 1985 the district court filed a written opinion on the merits. The court analyzed and interpreted the patent claims in view of the asserted changes to the Ti-Coating product. The court discussed the evidence presented on the defense of noninfringement, and applied the process claims and the product claims to the accused processes and structures. The court also reviewed a Patent and Trademark Office decision of February 27, 1985 denying reexamination, observing that "Claims 3 through 6 of patent '703 were interpreted by the PTO and the petition was denied", and discussed why "this Court will not follow the P.T.O.'s interpretation" of the claims. The district court found that Ti-Coating literally infringed claim 15 of the '703 patent and claim 21 of the '338 patent. Ti-Coating was held liable under the contract. (Neither party had cancelled the contract).

The district court referred the matter to a magistrate for an accounting. The magistrate recommended that SDC be awarded damages of $64,781.13 for the period between June 1, 1982 to November 1, 1982, and $140,700.80 for the period between November 1, 1982 to September 30, 1983. Those amounts would have been payable as royalties under the contract.

On September 26, 1985 the court entered final judgment on the award of $64,781.13. That judgment has been satisfied, and Ti-Coating's liability for that period is not further contested.

On December 5, 1985 the court entered final judgment awarding SDC $140,700.80, pursuant to Fed. R. Civ. P.

54(b). On the same day the court granted, on consent, SDC's earlier motion for leave to file a supplemental complaint seeking damages based on Ti-Coating's failure to pay royalties for its operations between October 1, 1983 and September 30, 1985, and allowed Ti-Coating to file an answer.

On December 19, 1985 Ti-Coating filed a notice of appeal to this court from the judgment awarding $140,700.80. A "protective" appeal to the Second Circuit was also filed, and we have been advised that it has been stayed by the Second Circuit pending our determination of appellate jurisdiction.

On January 21, 1986, after this appeal was filed, Ti-Coating filed its answer in the district court to SDC's supplemental complaint. That answer includes counterclaim counts for declaratory judgment of patent invalidity, unenforceability, and noninfringement.

SDC asserts that because the case does not arise under the patent law, the jurisdiction of the district court was not based on 28 U.S.C. § 1338, and therefore that the Federal Circuit does not have jurisdiction under 28 U.S.C. § 1295(a)(1). Ti-Coating, opposing SDC's motion to dismiss or transfer, asserts that § 1338 jurisdiction is based on the patent counts of its counterclaim, and thus that the appeal of all aspects of the case lies with the Federal Circuit.

ANALYSIS

I.

28 U.S.C. § 1295(a)(1) assigns to the Federal Circuit exclusive jurisdiction

> of an appeal from a final decision of a district court of the United States . . . if the jurisdiction

> of that court was based, in whole or in part, on section 1338 of this title . . . .

Section 1338 of Title 28 states in relevant part:

> (a) The district courts shall have original jurisdiction of any civil action arising under any Act of Congress relating to patents, plant variety protection, copyright and trade-marks. Such jurisdiction shall be exclusive of the courts of the states in patent, plant variety protection and copyright cases.

The issue is whether the case on appeal "arose" in the district court, in whole or in part, under an "Act of Congress relating to patents". The seemingly simple phrase "arising under" has engendered interpretation for at least a century.[1] Congress anticipated that it might also be necessary to interpret this court's jurisdictional mandate, as circumstances arose. The House Report on the Federal Courts Improvement Act of 1982 states:

> Should questions legitimately arise respecting . . . the direction of appeals in particular cases, the Committee expects the courts to establish, as they have in similar situations, jurisdictional guidelines respecting such cases.

H. R. Rep. No. 12, 97th Cong., 1st Sess. 41 (1981) ("House Report"). We and other courts have done so, as required. *Compare Air Products and Chemicals, Inc.* v. *Reichhold Chemicals, Inc.*, 755 F.2d 1559, 225 USPQ 121 (Fed. Cir. 1985) (jurisdiction in Federal Circuit); *Atari, Inc.* v.

---

[1] "Arising under" jurisdiction first appeared in the Act of March 3, 1875, 18 Stat. 470, the act that established a scope of federal question jurisdiction similar to that which exists today. As discussed in H. Shulman & E. Jaegerman, *Some Jurisdictional Limitations on Federal Procedure*, 45 Yale L.J. 393, 393 (1936), the distribution of judicial powers between federal and state courts was historically "politically . . . explosive".

JS & A Group, Inc., 747 F.2d 1422, 223 USPQ 1074 (Fed. Cir. 1984) (jurisdiction in Federal Circuit); *Chemical Engineering Corp.* v. *Marlo, Inc.*, 754 F.2d 331, 222 USPQ 738 (Fed. Cir. 1984) (jurisdiction in Federal Circuit) *with Beghin-Say International Inc.* v. *Ole-Bendt Rasmussen*, 733 F.2d 1568, 221 USPQ 1121 (Fed. Cir. 1984) (jurisdiction denied); *Gilson* v. *Republic of Ireland*, 787 F.2d 655, 229 USPQ 460 (D.C. Cir. 1986) (jurisdiction in D.C. Circuit); *Handgards, Inc.* v. *Ethicon, Inc.*, 743 F.2d 1282, 223 USPQ 214 (9th Cir. 1984) (jurisdiction in Ninth Circuit), *cert. denied*, 105 S. Ct. 963 (1985). The variety of procedural and substantive situations that occasioned those decisions required analysis not only of the words of the statute, but also of the intention of our congressional creators. This body of jurisprudence is now sufficiently evolved that we need not repeat its genesis; a few highlights will explain its application to this case.

In *Atari*, 747 F.2d at 1436, 223 USPQ at 1084, this court implemented Congress' concern that appellate jurisdiction be determined "at the complaint stage of the district court proceeding". This principle is of classical solidity with respect to determinations of original jurisdiction. For example, in *The Fair* v. *Kohler Die and Specialty Co.*, 228 U.S. 22, 25 (1913), the Supreme Court stated:

> [T]he party who brings a suit is master to decide what law he will rely upon and therefore does determine whether he will bring a 'suit arising under' the patent or other law of the United States by his declaration or bill. That question cannot depend upon the answer, and accordingly jurisdiction cannot be conferred by the defence even when anticipated and replied to in the bill.

See also Healy v. *Sea Gull Specialty Co.*, 237 U.S. 479, 480 (1915) ("Jurisdiction generally depends upon the case made and relief demanded by the plaintiff, and as it

cannot be helped, so it cannot be defeated by the replication to an actual or anticipated defence contained in what used to be the charging part of the bill.").

The complaint in the case at bar is for failure to pay royalties due under an existing patent license agreement. Such a suit has consistently been viewed as one arising out of state contract law, not "arising under" the patent law. As observed by the Supreme Court in *Luckett* v. *Delpark, Inc.*, 270 U.S. 496, 502 (1926):

> It is a general rule that a suit by a patentee for royalties under a license or assignment granted by him, or for any remedy in respect of a contract permitting use of the patent is not a suit under the patent laws of the United States, and can not be maintained in a federal court as such.

See also Pratt v. *Paris Gas Light & Coke Co.*, 168 U.S. 255 (1897); *Wilson* v. *Sandford*, 51 U.S. (10 How.) 99 (1850); *Beghin-Say International*, 733 F.2d at 1570-71, 221 USPQ at 1123.

Equally long-standing authority has held that raising patent-related defenses in the answer to a complaint does not create the "arising under" jurisdiction provided the district courts in § 1338, although these defenses may require application of the federal patent law. *See, e.g., American Well Works Co.* v. *Layne and Bowler Co.*, 241 U.S. 257, 260 (1916) ("A suit arises under the law that creates the cause of action."); *The Fair, supra.* In *C. R. Bard, Inc.* v. *Schwartz*, 716 F.2d 874, 879, 219 USPQ 197, 201 (Fed. Cir. 1983), this court stated "[i]t is well-settled that a case cannot 'arise under' federal law where the [patent] claim is merely a defense to a state court action." The fundamental nature of the action is not changed when it enters the federal system on the sole basis of diversity.

Having reached the federal system based on diversity, the case before us then became subject to patent counts of a counterclaim, that could not have been filed in the state court. A counterclaim, with its own jurisdictional predicate, normally generates its own responsive pleadings, and may remain in the suit even if the complaint is dismissed. Fed. R. Civ. P. 41(a)(2).

Adjudication of a patent counterclaim is the exclusive province of the federal courts. The patent counts of Ti-Coating's counterclaim, for declaratory judgment of patent invalidity, noninfringement, and unenforceability, are within the jurisdiction of the district court under § 1338. Under 28 U.S.C. § 1295(a)(1), when the district court's jurisdiction is based in part on § 1338, the appeal of the entire case, not solely the patent claims, lies in this court. Thus appellate jurisdiction over suits involving a § 1338 counterclaim is assigned to the Federal Circuit. However, this jurisdictional consequence requires something more than the mere filing, followed by the unopposed dismissal, of a counterclaim.

II.

When a § 1338 counterclaim is relied upon to establish appellate jurisdiction, it is subject to the same scrutiny as any other jurisdiction-controlling factor. The House and Senate Reports make clear that

> immaterial, inferential, and frivolous allegations of patent questions will not create jurisdiction in the lower court, and therefore will not create jurisdiction in the appellate court.

House Report at 41. *See also* S. Rep. No. 275, 97th Cong., 1st Sess. 19 (1981), *reprinted in* 1982 U.S. Code Cong. & Ad. News 11, 29 ("Senate Report"). The Senate expressed the concern that our jurisdiction not be manipulated "to create forum shopping opportunities between

the Federal Circuit and the regional courts of appeals on other claims", the Senate focusing on anti-trust issues as an example:

> Thus, for example, mere joinder of a patent claim in a case whose gravamen is antitrust should not be permitted to avail a plaintiff of the jurisdiction of the Federal Circuit . . . . Federal District judges are encouraged to use their authority under the Federal Rules of Civil Procedure . . . to ensure the integrity of the jurisdiction of the federal court of appeals by separating final decisions on claims involving substantial antitrust issues from trivial patent . . . counterclaims . . . raised to manipulate appellate jurisdiction.

Senate Report at 19-20, 1982 U.S. Code Cong. & Ad. News at 29-30. The Senate Report continued:

> The Committee intends for the jurisdictional language to be construed in accordance with the objectives of the Act and these concerns. If, for example, a patent claim is manipulatively joined to an antitrust action but severed and dismissed before final decision of the antitrust claim, jurisdiction over the appeal of the antitrust claim should not be changed by this Act but should rest with the regional court of appeals.

Id. at 20, 1982 U.S. Code Cong. & Ad. News at 30.

Ti-Coating asserts that its dismissed counterclaim was *bona fide* for purposes of determining our appellate jurisdiction, observing that the trial court refused to impose sanctions under Fed. R. Civ. P. 11 based on the absence of "clear evidence" that the counterclaim was made in bad faith. In this case, however, we need not decide whether the pleading of the patent counts of the counterclaim was *bona fide*, or whether the counts themselves

were trivial or substantial.[2] Ti-Coating's entire counterclaim was dismissed during the pleading stage. Since no objection was interposed by Ti-Coating, that dismissal was final and not appealable. Whatever the merits of its dismissal, the transient appearance of the counterclaim did not give it irrevocable control of the jurisdictional basis of the case. When the counterclaim including the § 1338 counts was dismissed on the pleadings, without opposition by the counter-claimant, it left no legacy on which to base appellate jurisdiction in this court.[3] *Accord Handgards*, 743 F.2d at 1285-88, 223 USPQ at 215-17 (where patent declaratory judgment claim was dismissed and not appealed in an earlier appeal, the Ninth Circuit retained jurisdiction over a subsequent antitrust appeal); *cf. USM Corp.* v. *SPS Technologies, Inc.*, 770 F.2d 1035, 1037, 226 USPQ 1038, 1039-40 (Fed. Cir. 1985) (where the patent issues were decided and thus disposed of by the Seventh Circuit prior to the creation of this court, we declined jurisdiction over a subsequent appeal of the remaining antitrust issue). Thus, the contract case on appeal, that reached federal district court solely on the basis of diversity, has not acquired a basis for jurisdiction arising in whole or in part under an Act of Congress relating to patents.

Accordingly, SDC's motion to transfer the appeal is *granted*. 28 U.S.C. § 1631.

IT IS SO ORDERED.

FOR THE COURT
/s/ Pauline Newman, Circuit Judge

Date: August 20, 1986

---

[2] Nor need we here consider such issues as compulsory versus permissive counterclaims, their relation to the defenses, or other questions raised by scholars as possibly affecting appellate jurisdiction.

[3] This result is unaffected by the further counterclaim pleaded in response to a further amended complaint; those subsequent procedures, after this appeal was filed, can not impart retroactive substance to the prior judgment here on appeal.

APPENDIX D

NOTICE OF MOTION UNDER F.R.CIV.P. 54(b) FOR RECONSIDERATION OF DECISION OF JULY 9, 1985 GRANTING PLAINTIFF'S MOTION FOR PARTIAL SUMMARY JUDGMENT ON ISSUE OF ROYALTY LIABILITY FOR NEW PRODUCT AND ANNEXED AFFIDAVIT

(United States District Court —
Southern District of New York)

(Filed September 16, 1985)
(Received and Entered September 24, 1985)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff, v. TI-COATING, INC., Defendant – 83 Civ. 9042 (LBS))

TOWNLEY & UPDIKE
Chrysler Building, 405 Lexington Avenue
New York, N.Y. 10174, Attorneys for Defendant

[HANDWRITTEN NOTATION]:

9/12/85 After consideration and oral argument, motion is denied.

So ordered.

/s/ *Leonard B. Sand*
U.S.D.J.

Copies Mailed to Counsel of Record *AK*

– MEMO ENDORSED –

APPENDIX E

OPINION

(United States District Court —
Southern District of New York)

(Dated July 9, 1985)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff, -against- TI-COATING, INC., Defendant – 83 CIV 9042 (LBS); HONORABLE LEONARD B. SAND, U.S.D.J.)

APPEARANCES: MORGAN, FINNEGAN, PINE, FOLEY & LEE, Attorneys for Plaintiff, 345 Park Avenue, New York, New York 10154, DAVID H. PFEFFER, ESQ., Of Counsel; TOWNLEY & UPDIKE, Attorneys for Defendant, 405 Lexington Avenue, New York, New York 10174, VINCENT BRICCETTI, ESQ., Of Counsel; FISHER, CRAMPTON, GROH & McGUIRE, Attorneys for Defendant, 877 S. Adams, Birmingham, MI 48011, Of Counsel.

SAND, J.

Plaintiff brings this action seeking to collect royalties under a licensing agreement on the products manufactured and sold by defendant which are alleged to have violated plaintiff's U.S. Patents Nos. 4,162,338 ('338) and 4,101,703 ('703). Partial summary judgment has already been granted establishing defendant's liability for royalties accruing prior to November 1982. Plaintiff has since moved for partial summary judgment of liability for royalties due under the same agreement for the period of November 1, 1982 to September 30, 1983. Defendant, however, contends that the coating used for the tools during the period was outside the scope of plaintiff's

patents, thus making plaintiff's claim for royalties invalid.

In an order dated January 28, 1985, this Court granted plaintiff's motion unless defendant subsequently submitted an offer of proof accompanied by affidavits supporting its contention that plaintiff's patents were not infringed. In response, defendant has submitted a portion of a deposition transcript of Charles Zichichi, president and principal stockholder of Ti-Coating, Inc., an affidavit by Andrew Pierce, an attorney, and a letter from John Blocher, Jr. to Zichichi, analyzing the relationship between Ti-Coating's production and the patents in question. On February 27, 1985, the U.S. Patent and Trademark Office ("P.T.O.") handed down a decision relating to a petition for reexamination of the plaintiff's patents brought by a third party. Claims 3 through 6 of patent '703 were interpreted by the P.T.O. and the petition was denied. We now reconsider plaintiff's motion for summary judgment in light of these submissions.

The patented invention which is the subject of this action is a three-layer coating for cutting tools and related industrial equipment to achieve increased durability. Prior to November 1982, defendant applied the patented three-layer coating directly to the wear surface of the tool. In November, however, defendant began to interpose a separate ½ to 1 micron thick layer of titanium nitride between the patented three layers and the substrate of the tool. Plaintiff claims that this additional layer is insignificant and that on the undisputed facts of the record, there is literal infringement of '703 patent, claims 15, 16 and 17, and of '338 patent, claim 21, as a matter of law. Defendant, however, fails to respond to this literal infringement claim and addresses its defense to the doctrine of equivalents. It contends that the new process does not infringe the plaintiff's patents which

specifically require the coating to be adjacent to the surface and that this presents a question of fact; therefore, summary judgment is inappropriate. Defendant cites the P.T.O. decision which, in its interpretation of '703 claims 3 through 6, required the three-layer coating to be adjacent to the substrate of the tool in order to violate the plaintiff's patent. For the following reasons, we conclude that literal infringement of '703 patent, claim 15, and literal infringement of '338 patent, claim 21, exists as a matter of law. Infringement of any one of these claims establishes liability for royalties under the licensing agreement.

DISCUSSION

Literal infringement of a patent requires that the infringer's device embody every element of the claim, *Builders Concrete, Inc.* v. *Bremerton Concrete Products Co.*, Appeal No. 84-1292, slip op. at 4 (Fed.Cir. Mar. 4, 1984), and summary judgment of this question is appropriate when no genuine issue as to any material fact exists which is necessary for resolution of the issue. *Chore-time Equipment* v. *Cumberland, Inc.*, 713 F.2d 774, 778-79 (Fed.Cir. 1983); *Molinaro* v. *Fannon/Courier Corp.*, 745 F.2d 651, 654 (Fed.Cir. 1984) (patent claim interpretation is an issue of law which does not preclude summary judgment). Plaintiff in this action asserts that Ti-Coating's operations fall squarely within the language of patent '703, claims 15, 16 and 17 and that literal infringement thus exists as a matter of law.

Patent '703, claim 15 describes "an article of manufacturing comprising:" (a) a hard metal substrate; and (b) a composite coating "including" the three patented layers. It is uncontested that Ti-Coating's product contains the three layers described in claim 15 in the proper order.

We therefore hold that literal infringement of the '703 patent, claim 15 exists as a matter of law.

Defendant Ti-Coating cites the testimony of its president, Mr. Zichichi, in an attempt to show that the patented three-layer tools and the infringing four-layer tools are not functional equivalents. Mr. Zichichi stated in his deposition that the additional layer decreased the brittleness of the tool and was therefore an improvement upon plaintiff's patented product.

Functional equivalence, however, does not bear on whether or not there is literal infringement. In *Graver Manufacturing Co.* v. *Linde Co.*, 339 U.S. 605 (1950), the Court held that literal infringement of a patent is determined by comparing the words of the patent claim with the accused device; if the device is within the claim, there is no infringement. 339 U.S. at 607. Patent claim 15 provides that infringement will occur when an item "includes" the three-layer coating. "[I]ncludes" is a broad word whose presence in the claim at issue herein results in literal infringement of the claim even where there is an intervening layer between the surface of the tool and the three-layer coating described in the claim. The accused device is one covered by the language of the patent and therefore infringement exists. Indeed, the defendant's own expert, Dr. John Blocher, Jr. in a letter to Ti-Coating President Zichichi, acknowledged that the word "include" as it appears in '703 claim 15 might result in literal infringement even where there is an intermediate coating between the substrate and the other layers. The defendant thus recognizes that the language in claim 15 is at the least problematic and at the most, as we hold, determinative.

It is clearly established in the law of patents that one cannot avoid infringement simply by adding an element to an already patented device. *Amstar Corp.* v. *Envirotech*

Corp., 730 F.2d 1476, 1483 (Fed.Cir. 1984); *A. B. Dick Co.* v. *Burroughs Corp.*, 713 F.2d 700, 703 (Fed.Cir. 1983). In this action, the only difference between defendant's coating and the patented coating is an extra layer placed adjacent to the wear surface of the tool. Once again, the case for literal infringement stands.

Our conclusion is also supported by an examination of the language used elsewhere in patent '703. Such an examination reveals that plaintiff was able to express the concept of layering coatings on top of each other and directly touching the substrate of the tool, by using phrases such as "continguous [*sic*] with," "adjacent," "adjoining" and "in direct contact with." A broader concept clearly attaches to the use of the word "including" in claim 15. The language in claim 15 allows for the intervening layer of titanium nitride inserted by the defendant and defendant has therefore infringed plaintiff's patent '703, claim 15 as a matter of law.

Finally, the defendant offers the affidavit of attorney Andrew Pierce which states that the four-layer coating currently being utilized by Ti-Coating is an improvement over the patented three-layer coating. There are two problems with this submission. First, Pierce lacks personal knowledge of Ti-Coatings products and production techniques and merely reiterates in his affidavit the unsworn testimony of defendant's employee. An attorney's interpretation of subjective information is not persuasive authority. Second, Pierce's attempt to establish the additional layer as an improvement goes to functional equivalence, which is irrelevant to determining literal infringement. *Graver Manufacturing Co.* v. *Linde Co.*, *supra*. The Pierce affidavit therefore does not alter the conclusion of this Court with respect to defendant's literal infringement of claim 15.

We recognize that Patent '703, claims 16 and 17 contain language that is somewhat narrower than claim 15. Claim 16 provides for various layers "covering" one another and for these layers to be "covering" the wear surface of the tool. Claim 17 provides that the various layers be "overlying" one another and that such layers be "overlying" the surface of the tool. Each patent claim, however, defines a separate invention *Jones* v. *Hardy*, 727 F.2d 1524, 1528 (Fed. Cir. 1984), and must be separately considered, *W. L. Gore & Associates, Inc.* v. *Garlock, Inc.*, 721 F.2d 1540, 1559 (Fed.Cir. 1983). In light of our conclusion that patent claim 15 allows for the intervening layer inserted by the defendant and has thus been literally infringed, it is not necessary for this Court to determine whether claims 16 and 17 have been literally infringed as well.

While patent '703 protects the product of the three-layer coating, patent '338 protects the process by which the coating is produced. Plaintiff alleges that claim 21 of this patent has also been literally infringed as a matter of law; we agree. Ti-Coating's process includes every step of the patented process but employs an additional step to produce the fourth layer. As in the case of product claims, however, "the mere addition of a step to a process that otherwise infringed a patent does not negate infringement." *Bandag, Inc.* v. *Lewis General Tire Co.*, 207 U.S.P.Q. 745, 756 (W.D.N.Y. 1980). We therefore conclude that patent '338 claim 21 has been infringed by defendant as a matter of law.

The practice of a single valid patent claim is sufficient to establish Ti-Coating's royalty liability. (Licensing Agreement 4(d)). Ti-Coating has infringed at least two

of the patentee's claims; it is therefore liable to plaintiff for royalties.[1]

The P.T.O. decision of February 27, 1985, denying a third party's petition for reexamination of the plaintiff's patent, interpreted claims 3-6 of patent '703. The language of these claims is very similar to the language of claims 15-17 of '703, the claims at issue here. The P.T.O. interpreted the language of patent claims 3-6 as not contemplating the addition of an intermediate layer between the substrate of the tool and the plaintiff's patented three-layer coating. While we acknowledge that the language of claims 3-6 is almost identical to the language of claims 15-17, this Court will not follow the P.T.O.'s interpretation for the following reasons.

As an initial matter, we note that the P.T.O. does not have an estoppel or other legally binding effect on this Court especially where, as here, the statements of the

---

[1] Since summary judgment can be granted because of Ti-Coating's literal infringement of patents '703 and '338, this Court need not decide whether a suit can be maintained under the doctrine of equivalents. *Graver Manufacturing Co.* v. *Linde Co.*, 339 U.S. 605, 608-9 (1950) sets forth a tripartite test under which a patentee can maintain infringement under the doctrine of equivalents. The device must "perform substantially the same function in substantially the same way and accomplish substantially the same result . . . ."

The defendant argued that the additional layer decreases the brittleness of the tool, an unfortunate side effect of the layered coatings. Plaintiff countered with arguments that the additional layer serves no significant purpose. To support this contention, plaintiff cites the fact that Ti-Coating neither advertised the change in formula nor notified 97% of its customers of the change. Next, plaintiff argued that even if the additional layer does increase the durability of a tool, that it, plaintiff, holds the patent for tools with increased durability. The accused tools would therefore be a "colorable variation" of the patented tools.

The doctrine of equivalents requires resolution of factual issues which are not appropriately decided on summary judgment. Because literal infringement has been demonstrated in this case as a matter of law, however, this Court need not decide the equivalence issue and plaintiff is entitled to summary judgment in its suit for royalties.

P.T.O. are made in a determination upholding a decision declining to reexamine an already issued patent, in a proceeding in which the patentee was not a party and, under P.T.O. rules, could not participate. A court, in evaluating the validity of a patent, must give "due respect" to P.T.O. decisions but is not bound thereby. *Lindemann Maschinenfabrik* v. *American Hoist and Derrick Co.*, 730 F.2d 1452 (Fed.Cir. 1984). Furthermore, the case law suggests that courts should defer to the Patent Office in areas of that office's expertise. *Carter-Wallace, Inc.* v. *Riverton Laboratories, Inc.*, 304 F.Supp. 357, 372 (S.D.N.Y. 1969); *see also Brenner* v. *Manson*, 383 U.S. 519, 531-32 (1950) (Court deferred to P.T.O. determination on patent utility stating that it would not overturn P.T.O.'s finding in a "technical area"); *Goodyear Tire and Rubber Co.* v. *Ladd*, 349 F.2d 710, 711 (D.C.D.C. 1965) (P.T.O.'s expertise in technical areas such as "obviousness" require affirmance of its judgments). This presumption of the validity of P.T.O. determinations, however, is not absolute. In cases where the evidence before the Court is insufficient to support the P.T.O. decision, the court must rule in accordance with the evidence. *Wagner* v. *Reynolds*, 241 F.Supp. 910 (D.D.C. 1965). In addition, the deference to be accorded to a P.T.O. determination applies mainly to issues of fact. *Sampson* v. *Ampex Corporation*, 333 F.Supp. 59 (S.D.N.Y. 1971); claim interpretation is an issue of law. *Molinaro* v. *Fannon/Courier Corp.*, 745 F.2d 651, 654 (Fed.Cir. 1984). Given the fact that the word "including," both on its face and when compared with other language utilized in the patent, would permit insertion of additional layers between the tool surface and the three-layer coating, this Court will adhere to its previous determination that defendant's use of additional layers does not avoid its literal infringement of plaintiff's patent claims.

For the above reasons, this Court finds literal infringement of patent '703 claim 15 and of patent '338 claim 21 and therefore grants plaintiff summary judgment on the issue of royalty liability.

The matter is referred to Magistrate Leonard Bernikow, or such Magistrate as he shall designate, to report and recommend as to damages for the period November 1, 1982 to September 30, 1983 as well as the period June 1 to November 1, 1982. Plaintiff's motion for summary judgment as to the earlier period is similarly referred to such Magistrate.

SO ORDERED.

/s/ LEONARD B. SAND
U.S.D.J.

Dated: New York, N.Y.
July 9, 1985

APPENDIX F

LICENSE AGREEMENT BETWEEN SCHWARZKOPF DEVELOPMENT CORPORATION AND TI-COATING, INC.

This License Agreement, effective as of June 1, 1982, is made by and between Schwarzkopf Development Corporation ("SDC), a Maryland corporation having its principal place of business in New York, New York, and Ti-Coating, Inc. and Ti-Coating of Texas, Inc., respectively, a Michigan corporation having its principal place of business at 42123 Irwin, Mt. Clemens, Michigan 48045 and a Texas [*Michigan**] corporation having a principal place of business at 8641 Wayfare, Houston, Texas 77075 (collectively referred to as "LICENSEE").

1. *LICENSED PATENTS.* Rights under United States Patent No. 4,101,703, issued July 18, 1978, entitled "Coated Cemented Carbide Elements", and United States Patent No. 4,162,338, issued July 24, 1979, entitled "Coated Cemented Carbide Elements and Their Manufacture", are licensed by SDC to LICENSEE by this agreement.

2. *WARRANTY.* SDC warrants that it is the owner of the entire right, title and interest in the United States Patent Nos. 4,101,703 and 4,162,338 and that it has the right to grant this license.

3. *LICENSE.*

(a) SDC hereby grants to LICENSEE, and its wholly owned subsidiaries, upon the terms and conditions set forth in this agreement, a non-exclusive license to practice, by making, having made

---

* *Printer's note:* Bracketed insertions indicate initialled, handwritten changes on original copy.

using and selling, the inventions claimed in United States Patent Nos. 4,101,703 and 4,163,338.

(b) This agreement does not grant to LICENSEE any express or implied rights or any immunity from suit in any foreign country in which SDC, or any company affiliated with SDC, also possesses patent rights.

(c) This agreement does not grant to LICENSEE the right to grant sub-licenses.

4. *ROYALTIES.*

(a) In consideration for the rights granted by SDC to LICENSEE under this agreement, LICENSEE agrees to pay to SDC, in the manner provided in this paragraph 4, a royalty computed as follows:

(i) On articles manufactured under the license which are comprised of tools and parts supplied by others, for which LICENSEE charges a fee for coating with either titanium nitride overlying titanium carbide, or titanium nitride overlying titanium carbonitride overlying titanium carbide, *except for cutting inserts for tools,* ten percent (10%) of the price charged by LICENSEE for services performed on such tools and parts by or on behalf of LICENSEE.

(ii) On articles manufactured under the license which are cutting inserts for tools, whether manufactured in their entirety by LICENSEE or provided by others for coating by LICENSEE, a royalty of:

(A) five percent (5%) of the annual net sales value of cutting tool inserts manufactured under the license, up to the first $100,000.00 in annual net sales value;

(B) three percent (3%) of the annual net sales value of cutting tool inserts manufactured under the license in excess of

$100,000.00 up to $300,000.00 in annual net sales value; and

(C) two and one-half percent (2½%) of the annual net sales value of cutting tool inserts manufactured under the license in excess of $300,000.00 in net annual sales value.

(b) "Net sales value" for any coated cutting tool insert shall mean the price at which LICENSEE's customer lists that coated insert for sale to the trade in its then current price list. If no such price list exists, then the sales price listed for the most similar cutting insert in terms of size, quality and coating, that appears in the then current price list of one or more of Kennmetal, Inc., Carmet Company or the V. R. Wesson Division of Fansteel, Inc., F. O. B. a factory or sales office in the United States located east of the Mississippi River.

(c) "Annual net sales value" shall be the aggregate in any calendar year of the "net sales value" of coated cutting tool inserts computed in accordance with paragraph (b) hereof. The period from September [*June*] 1, 1982 through December 31, 1982 shall be considered a calendar year for purposes of this paragraph (c).

(d) "Article manufactured under the license" shall mean an article which embodies an invention claimed in United States Patent No. 4,101,703 or which is made by or with the use of any method embodying an invention claimed in United States Patent No. 4,162,338.

(e) Within thirty days after each three month period, commencing with the period beginning September [*January*] 1, 1982 [*1983*], LICENSEE shall transmit to SDC a report stating the quantities of articles coated or otherwise manufactured, used and sold

under this agreement, and a computation of the royalties due under this agreement. Royalties due for the period from December [*June*] 1, 1982 through December 31, 1982 shall be reported with the royalties due for the period from January 1, 1983 through March 31, 1983. Simultaneously with the transmittal of each report, LICENSEE shall pay to SDC the royalty due for the period covered by the report. If no royalties are due, LICENSEE shall so report.

(f) In the event that the aggregate royalties paid by LICENSEE to SDC in any calendar year after 1982 are less than the minimum amount of $5,000.00, and LICENSEE does not pay to SDC an amount equal to the deficiency within 30 days after the end of such calendar year, SDC may at its election, terminate this agreement upon 30 days' notice.

(g) It is understood that the royalty rates computed pursuant to Section 4 hereof have been aggregated for the convenience of LICENSEE. Upon expiration of U.S. Patent No. 4,101,703, the said royalty rates shall decrease by fifty percent (50%).

5. *RECORDS.* LICENSEE agrees to maintain complete and accurate books and records containing all information necessary for the purposes of calculating and verifying the royalties due to SDC under this agreement. These books and records shall be available for inspection, during regular business hours and upon reasonable notice, by an independent certified public accountant retained by SDC for the purpose of verifying LICENSEE's royalty reports. Such inspection shall not be conducted more than once a year, nor after six months from the date of termination of this License Agreement. Information concerning such royalty payments shall be maintained in confidence by SDC, except insofar as is necessary to enforce SDC's rights under this License Agreement.

6. *PAST INFRINGEMENT.* Upon execution of this agreement, SDC hereby releases LICENSEE from all past claims for infringement of United States Patent Nos. 4,101,703 and 4,162,338 arising out of products manufactured, used or sold by LICENSEE. The release granted herein also applies to customers of LICENSEE but only with respect to products coated by LICENSEE.

7. *ASSIGNMENT.* This agreement may not be assigned by LICENSEE without the prior written consent of SDC except that this agreement may be assigned, without the consent of SDC, to the successor to that part of the LICENSEE's business to which this agreement relates.

8. *TERMINATION.*

(a) If LICENSEE becomes bankrupt or insolvent, or if the business of LICENSEE is placed in the hands of a receiver, assignee or trustee, whether voluntarily or involuntarily, this agreement shall immediately terminate.

(b) Except as specified in paragraph 4(f) hereof, upon any breach or default by LICENSEE under this agreement, SDC may terminate this agreement by notifying LICENSEE by registered mail and specifying the breach of default. This agreement shall terminate 30 days after receipt of such notice by LICENSEE, unless LICENSEE in the interim shall have cured such breach of default.

(c) Upon termination of this agreement, LICENSEE shall not be relieved of duties and obligations under this agreement accrued prior to termination, including the obligations to account for and pay royalties on products made, used or sold prior to termination.

(d) This agreement shall remain in force until the expiration date of U.S. Patent No. 4,162,338 unless sooner terminated under the provisions hereof.

(e) LICENSEE may terminate this agreement at any time by notifying SDC by registered mail. This agreement shall terminate 30 days after receipt of such notice by SDC.

9. *CHOICE OF LAW.* This agreement shall be interpreted in accordance with the laws of the State of New York.

10. *COMMUNICATIONS.* All communications, reports and remittances sent or required to be sent pursuant to this agreement, shall be deemed properly sent if transmitted by certified mail, return receipt requested, postage prepaid, to SDC or LICENSEE at the following addresses:

Schwarzkopf Development Corporation
595 Madison Avenue
New York, New York 10022
Attention: Ronald Altman, Chairman

Ti-Coating, Inc.
42123 Irwin
Mt. Clemens, Michigan 48045
Attention: Charles Zicchichi [*sic*], President

11. *MOST FAVORED LICENSEE.* In the event that SDC hereafter grants any license under the LICENSED PATENTS which license calls for payment of running royalties and in the aggregate, considering all of its terms and conditions, is more favorable to the LICENSEE than the terms of this agreement, LICENSEE may, at its option, elect to thereafter be given the benefit of the more favorable license, in its entirety.

ATTEST:
/s/ [*Illegible*]

SCHWARZKOPF DEVELOPMENT CORPORATION
By: /s/ Ronald Altman, Its Chairman

ATTEST:
_____

TI-COATING, INC.
By: /s/ Charles Zichichi, Its President

ATTEST:
/s/ Rose Marie Zichichi, V. Pres.

TI-COATING OF TEXAS, INC.
By: /s/ Charles Zichichi, Its President

APPENDIX G

UNITED STATES PATENT 4,101,703

United States Patent [19] [11] 4,101,703
Schintlmeister [45] Jul. 18, 1978

---

[54] COATED CEMENTED CARBIDE ELEMENTS

[75] Inventor: Wilfried Schintlmeister, Reutte, Austria
[73] Assignee: Schwarzkopf Development Corporation, New York, N.Y.

[21] Appl. No.: 571,695 [22] Filed: Apr. 25, 1975

Related U.S. Application Data

[63] Continuation of Ser. No. 329,128, Feb. 2, 1973, abandoned.

[30] Foreign Application Priority Data

Feb. 4, 1972 [AT] Austria 896/72
Jul. 21, 1972 [AT] Austria 6317/72

[51] Int. Cl.[2] B32B 15/04; B32B 9/04
[52] U.S. Cl. 428/216; 148/31.5; 428/420; 428/457; 428/539
[58] Field of Search 428/420, 457, 539, 216; 148/31, 5

[56] References Cited

U.S. PATENT DOCUMENTS

3,642,522	2/1972	Gass et al.	117/106C
3,656,995	4/1972	Reedy	117/69
3,684,585	8/1972	Stroup et al.	148/6
3,771,976	11/1973	Wakefield	29/194

Primary Examiner — James R. Hoffman
Attorney, Agent, or Firm — Morgan, Finnegan, Pine, Foley & Lee

[57] ABSTRACT

Cemented carbide elements with working faces bearing a thin multilayer or stratified coating of nonuniform composition of wear-resistant materials exhibit superior wear-resistance for improved performance and service life under severe service conditions as in the case of inserts for cutting tools and wire drawing dies. In one embodiment, an initial carbon-rich layer of titanium carbide or carbonitride coating material in direct contact with a cemented carbide part or insert underlies a middle or intermediate stratified transition zone made up of a series of parallel layers or strata of coating material wherein the content of carbon and nitrogen is not constant but varies with the stratum or location by depth in that zone with the material gradually changing to titanium compounds that are progressively lower in combined carbon content and richer in nitrogen than in the initial layer until the composition of the outermost stratum of the transition zone approximates that of the overlying surface layer of high nitrogen content (e.g., titanium nitride). The coating is formed by a gas deposition method wherein changes in the concentration of gaseous carbon and nitrogen compounds are used to control the formation of the various layers of different composition in the layered coating.

19 Claims, No Drawings

COATED CEMENTED CARBIDE ELEMENTS

This is a continuation of application Ser. No. 329,128 filed Feb. 2, 1973 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with protective coatings for wear-resistant elements intended for severe operating

conditions and with methods of depositing such coatings on the wear-resistant substrates or inserts.

2. Prior Art

Cemented carbides, also known as sintered carbides, are solid and coherent masses made by pressing and sintering a mixture of powders of one or more metallic carbides and a much smaller amount of an iron group metal, such as cobalt, to serve as a binder metal. These carbides may be used as tools or inserts for machining, milling, blanking, and drawing operations; also as shaping dies, spinning dies, and for many other applications. Such tools are capable of performance beyond the limits of high speed steels and in many cases are suitable for use on very hard abrasive materials and on tough alloys. Cemented carbides are widely used for structural parts and tools subject to intense wear or other service loads that require high compressive strength. Suitable carbides for such purposes include the carbides of tungsten, titanium, tantalum, columbium, molybdenum, vanadium, chromium, zirconium, and hafnium.

Cemented carbides because of their unique strength and hardness are frequently subjected to conditions of intense wear. The manner and rate of wear depends very largely on the use and service conditions of the cemented carbide part. Wear is frequently caused by mechanical abrasion which can be greatly intensified by diffusion processes when operating at elevated temperatures. Corrosion is also a cause in the wear of such parts, for example, when cemented carbide is used in corrosive media or when oxidation in the air takes place at elevated temperatures. When cemented carbides are used for shaping of other parts, either by machining and nonchipping shaping operations or by other processes, the cemented carbide parts are not only subjected to heavy mechanical

stresses but there is frequently also intense heating which greatly accelerates the wear.

In the machining of long-chipping and short-chipping materials, as for example, steel or cast iron, respectively, wear on the cutting edge can our [*sic*] as a result of cratering of the rake face and abrasion of the clearance face. Furthermore, the chips can adhere or weld onto the cutting edge of the part and cause chipping or splintering of the edge. In interrupted cuts, crack formation may be caused by rapid temperature changes and splintering can occur from heavy impacts.

It has now been discovered that wear-resistant stratified coatings composed of a number of layers of certain different compositions provide a number of significantly improved results of an unpredictable nature as described hereinafter, particularly when these coatings are employed as protective wear-resistant coatings on cemented carbide substrates and other hard material bases. The coated articles have many uses for metal working and other purposes that involve exposure to mechanical wear and abrasion.

SUMMARY OF THE INVENTION

The present invention relates to a hard-wear resistant multilayer coating of nonuniform composition in adjoining layers and wherein said coating contains at least two different wear-resistant materials and includes at least two elements of the group consisting of carbon, nitrogen, boron and silicon in chemical combinations with titanium. It also encompasses articles with such coatings on hard material bases or substrates of the type described hereinafter, and especially cemented carbides substrates having an adherent coating that contains at least two different wear-resistant materials and includes carbon and nitrogen in chemical combination with titanium.

This invention also encompasses a method of making the aforesaid articles by decomposition onto substrates from reactive gaseous mixtures under controlled reaction conditions, including the composition of the gaseous mixtures.

Other aspects of the invention involve one or more of such features as the structure of the multilayer (i.e., more than one layer) article and the thickness and disposition or location of its layers, especially carbon-rich layers composed of material of a substantial or high carbon content and a lower nitrogen content, as well as nitrogen-rich layers of material containing less carbon than nitrogen.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The coated articles of the invention may employ as a base or substrate any hard solid material to which the coatings will adhere. These hard materials are generally hard metals or alloys thereof, including metal-like alloys, compositions or materials. Thus, the substrates may be cermets and like products of powder metallurgy, as well as hard metal carbides and/or nitrides, etc. and alloys, such as cobalt-chromium-tungsten, superalloys and other alloys employed in high speed cutting tools. In general, sintered materials are preferred as substrates, especially the wear-resistant cemented carbides. Among the many suitable base or substrate materials, cemented tungsten carbide compositions containing about 5-30% of a binder metal of the iron group (cobalt, iron, and/or nickel) have been used with excellent results, and up to a total of 40% of the tungsten carbide content may be replaced by one or more other carbides, including those of titanium, tantalum, niobium, vanadium or chromium. Cemented carbides containing from 60-90% titanium carbide with the balance being nickel or a nickel-molybdenum alloy binder

are also used and up to half of this titanium carbide may be replaced by titanium nitride.

A coating of the present invention is characterized by a multilayer structure, often so thin that the total thickness of the coating is less than 10 or 20 microns, as well as the fact that its chemical composition is not uniform or homogeneous although its physical appearance is typically homogeneous with no strata visible even under a microscope. These coatings are made up of two or more layers, and at least two of the layers are of different composition in respect to having either different chemical components or different proportions of the same components or elements. The principal constituents of the coatings are metal compounds of at least two nonmetals of the group consisting of carbon, nitrogen, boron and silicon, of which carbon and nitrogen are generally preferred. But also compounds of nonmetals, such as boron carbide, boron nitride and silicon carbide, can be used. Titanium may be utilized as the sole metallic component of such compounds; also it is contemplated that it may be associated with considerable amounts of compounds of one or more other metals in Groups III, IV, V and VI of the Periodic Table of Elements that have atomic numbers in the range of 21 to 74. Thus, one may also employ compounds of one or more of such metals as chromium, molybdenum, tungsten, scandium, yttrium, lanthanum, zirconium, hafnium, vanadium, niobium and tantalum, usually in lesser total amount so that the titanium constitutes a major portion or more that [*sic*, than] 50% of the total weight of the chemically combined metals in the coatings. In some cases it may be also useful to substitute more than 50% of the titanium. If coatings have particularly great ductility are required, then additions of iron, cobalt, or nickel, or molybdenum, or mixtures thereof up to about 20% of the total coating weight are advantageous. While the specific description hereinafter is directed entirely at coatings

composed of titanium compounds and their decomposition for the purposes of a full and detailed disclosure of materials that have provided greatly improved results, such description is generally applicable to coatings which also contain the compounds of the aforementioned other metals and nonmetals.

In respect to the contents of nonmetals in the titanium compounds in the coatings of this invention, a nitrogen or carbon content of more than 14% by weight is regarded as a high nitrogen or high carbon content. Amounts of these elements below 6% are considered low contents, and the intermediate range of 6-14% may be called an average or medium content of carbon or nitrogen. On the other hand, the expressions "carbon-rich" and "nitrogen-rich" herein are intended to denote coating deposits wherein carbon or nitrogen, respectively, constitutes a major proportion of the total weight of the combined nonmetals in the particular deposits and also to denote gaseous mixtures containing enough carbon-containing or nitrogen-containing gas material to produce such solid deposits. In general, this means that a solid deposit has a carbon or nitrogen concentration, respectively, that is either a high content or in the upper half of the intermediate content range, say above 10%.

In general, the chemical compositions of each of the various layers or strata are substantially uniform in their planar dimensions, that is across the entire width and length of their areas, by reason of the manner of their deposition from the vapor state onto solid bases or substrates as described hereinafter; instead of the desired and significant differences in composition occur through the depth or thickness of the coating, and the composition of one principal layer is different from the adjoining overlying or underlying layer; and this difference in composition may be slight and progressive in gradations through a

transition zone having many ultra-thin strata in some instances or a more pronounced change in other cases.

The arrangement, thickness and composition of the individual layers will depend upon the surface conditions of the wear part. For instance, these may consist of several different layers, namely pure titanium carbide, titanium carbonitrides of medium to high carbon content, pure titanium nitride or titanium carbonitrides with a high nitrogen content. In some cases, it may be advantageous to have five or more layers while in other cases, two principal layers may be sufficient, for example, a carbon-rich layer and a nitrogen-rich layer of titanium compounds. The individual layers can be either contiguous or there may be an intermediate stratified transition zone wherein the intermediate layers or strata have variable carbon and nitrogen contents; that is, the combined carbon content is decreasing and the combined nitrogen content increasing in one direction through the thickness of that zone (e.g., away from the substrate and toward the exterior surface of the composite coating), and the carbon is increasing and nitrogen decreasing in the other direction (e.g., toward the substrate). Such changes in composition may be essentially continuous or very gradual in such a transition zone wherein the composition is changed from a composition similar to that of a principal layer on one side of the zone to a composition similar to that of a different principal layer on the other side of the zone. On the other hand, the change in composition may be very marked as at the single interface of two contiguous carbon-rich and nitrogen-rich coating layers.

The thickness of a transitional carbonitride layer or zone may be about 0.1 to 10 microns. The individual or principal layers of titanium nitride and titanium carbonitride having medium to high nitrogen content, are usually present in thickness of about 0.3 to 30 microns. The indi-

vidual or principal layers of titanium carbide and titanium carbonitride having a low nitrogen content are usually present in thicknesses of 0.2 to 20 microns.

In many cases, it has been found advantageous to have a layer structure in which the layer or stratum with the maximum carbon content is located close to the base or substrate surface and remote from the external surface of the coating, whereas the layer or stratum of maximum nitrogen content is located close to the surface of the coating, and remote from the substrate. For example, the layer near the base may consist of titanium carbide or a titanium carbonitride and the layer near the surface of the coating of titanium nitride. The coating can be formed in such a manner that a pure titanium carbide layer is joined to a pure titanium nitride layer by means of a series of carbonitride layers in a transition zone that provides a gradual and continuous change in composition from carbide to nitride.

The formation of the coating layers in accordance with the present invention can be most simply carried out by use of a gas phase deposition. However, other well known methods such as plasma spraying, sputtering, or pack cementation have also been found useful.

Gas phase deposition has the particular advantage that the layer composition can be readily controlled by regulation of the composition, the pressure and temperature of the gas phase. The composition of the gas phase can easily be adjusted by addition of suitable gaseous compounds. Furthermore, the mixing ratio of the gas phase may also be varied during the deposition process in a simple manner which causes a corresponding change in the deposited coating composition. The cemented carbide parts may be cleaned by conventional techniques prior to applying the coating material. Surface carburization of the cemented carbide substrates may also be carried out where the car-

bon content of the cemented carbide is too low for effective coating with the hard materials of this invention.

Atmospheric pressure may be employed for the gas deposition of all the coating materials as in the examples that follow, but it is also contemplated that it may be desirable to employ higher or lower pressures in some instances. For example, it may be advantageous to employ subatmospheric pressures for depositing coatings of titanium carbide, and it is also contemplated that titanium nitride deposits may be formed with a gaseous mixture at superatmospheric pressures. Suitable operating temperatures for the preferred titanium compounds of carbon and nitrogen are in the 700° to 1200° C. range.

The gas mixture is varied depending upon the composition of the layer desired to be deposited. Generally, in order to form a pure titanium nitride layer, the gas mixture comprises a titanium halide, for example, titanium tetrachloride; nitrogen or gaseous nitrogen compounds such as ammonia, and similar nitrogen compounds. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof.

In order to form titanium carbonitride layers, a gas mixture preferably comprises a titanium halide, a hydrocarbon gas, and nitrogen or a gaseous nitrogen compound, such as, aniline, pyridine, aliphatic and aromatic amines and similar organic nitrogen compounds. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof.

In order to form a pure titanium carbide layer, the gas mixture may comprise a titanium halide, and hydrocarbon gas. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof. Other sources of carbon for the processes are the vapors of organic halides of either the aliphatic or aromatic type.

According to the present invention, there is provided a new coating for cemented carbide parts which reduces abrasion and cratering of the surfaces of the cemented carbide tool inserts to a surprising and outstanding degree. This is in marked contrast with results that have been obtained with tool inserts bearing a coating of uniform composition. For instance, special cutting disposable inserts and tips made of cemented carbides for machining parts have recently been developed, and these have a wear-resistant surface coating of titanium carbide. Such disposable cutting inserts, e.g., coated with titanium carbide, generally have had two to three times the service life of similar uncoated disposable tips when used under comparable machining conditions. However, their service life is limited by the cratering type of wear although the clearance face wear is relatively slight.

It has been proposed in the U.S. Pat. No. 3,717,496 to coat cemented carbide inserts with titanium nitride or titanium carbonitrides in order to reduce wear. In practice it was found that titanium carbide produces better protection for the clearance face, whereas titanium nitride provides higher resistance to cratering, but the clearance face wear is 2 or 3 times greater than with a comparable insert coated with titanium carbide. Accordingly, in the case of titanium nitride coatings, the great clearance face wear frequently causes failure of the inserts before marked cratering has occurred; hence, the improved cratering resistance could not even be utilized.

It has now been discovered that the coatings of the present invention which may consist of different or alternating layers rich in titanium combined with nitrogen and carbon, respectively, impart a much greater wear-resistance in cutting tools than a uniform coating composition of either alone. While the cause for this is not completely understood, this phenomenon is probably due to

the fact that each of the layers react differently to the different types of wear. As previously mentioned, the clearance face wear in cutting tools is predominantly due to abrasion, while the cratering wear is primarily due to diffusion. If part of a tool coated according to this invention is subjected to one of such types of wear, it is thought that if the uppermost layer contains a composition with little resistance to this type of wear, it will be rapidly abraded and thus expose the next layer having a different composition which is more likely to be highly resistant to this type of wear. Moreover, the combination of the different layers provides surprising and improved results as mentioned hereinafter.

An important advantage of the combination of layers of the new coatings is that they have a less pronounced epitaxial structure and a finer grain structure, and this reduces possibility of cracking and chipping of the layers.

Additional advantages are found when the new coated tool elements are subjected to interrupted cuts, particularly in milling, for they display greater resistance to cyclical temperature changes and to impact effects.

The structure of the coating layers of the present invention is not only of significance for cutting tools, but is equally advantageous for tools used for non-chipping, shaping operations, e.g., for drawing, swaging, or forging.

When drawing thick steel wire using drawing dies coated with titanium carbide alone it has been found that the titanium carbide is highly resistant to the large tensile forces exerted on the surface of the drawing die bore; however, galling of the wire was observed relatively early. The formation of undesirable grooves in the wire was found to be due to peeling of the titanium carbide coating.

When drawing dies were equipped with the combined titanium carbide-titanium nitride coating of this invention, there appeared to be a substantial reduction in the coefficient of friction, for the drawing force was reduced; consequently the service life was increased compared with the comparable drawing dies having only a pure titanium carbide coating. This reduction of the drawing force also makes it possible to effect larger reductions in a single pass.

The following examples illustrate the practice of the invention.

EXAMPLE I

Cemented carbide plates (84% tungsten carbide, 10% titanium and tantalum carbides with 6% cobalt as a binder metal) or drawing dies (tungsten carbide containing 6% cobalt as a binder metal) which are to be coated are first cleaned and then carburized in order to enrich the surface with carbon. The cemented carbide parts are then annealed at 850° to 1200° C. in a gas mixture consisting of 92.3 volume % of hydrogen, 0.4% titanium tetrachloride, 7% methane and 0.3% nitrogen. The gas mixture reacts at the surface of the cemented carbide part and forms an initial titanium carbonitride deposit with a high carbon content. After 5 to 20 minutes, the flow of methane is slowly reduced and that of the nitrogen increased over a period of 10 to 40 minutes. After this operation, the parts are coated for 20 to 60 minutes in a gas mixture consisting of 0.5% titanium tetrachloride, 69.5% hydrogen and 30% nitrogen, which yields a final layer of pure titanium nitride.

Metallographic examination of the coatings showed that, depending upon the process parameters (temperature, time and gas composition), the coatings comprise a 0.5 to 3 microns thick initial layer of titanium carbonitride

of high carbon content (80% titanium 18% carbon and 2% nitrogen) in contact with the carburized cemented carbide substrate, and the composition of the deposited material changes gradually to provide a 3 to 20 microns thick surface layer of titanium nitride. Since titanium carbide and titanium nitride are miscible in any proportions, sharp boundaries between the individual layers in the coating cannot be observed.

EXAMPLE II

Cemented carbide tips (71% tungsten carbide, 20% titanium and tantalum carbides with 9% cobalt) or drawing dies (tungsten carbide containing 9% cobalt binder) to be coated are first cleaned and may be subsequently carburized in order to enrich the surface with carbon. The parts are then annealed at 850° to 1200° C. in a gas mixture consisting of 0.4 volume % of titanium tetrachloride, 10% methane, 0.2% nitrogen and the remainder of hydrogen. The gas mixture reacts at the surface of the cemented carbide parts resulting in the deposition of a titanium carbonitride of high carbon content. After 5 to 20 minutes, the proportion of methane is slowly reduced, while that of nitrogen is increased during a transition deposition period of 30 to 60 minutes. The parts are further coated in a gas mixture consisting of 0.4% by volume of titanium tetrachloride, 1.2% methane, 74% hydrogen and 25% nitrogen, with the nitrogen content now higher than the methane content, for another 20 to 60 minutes, with the result, that a titanium carbonitride layer of high nitrogen content is now deposited. Atmospheric pressure is employed in all of the foregoing treatments and in all other detailed examples herein.

Metallographic examination of the coatings showed that, depending on the process conditions, each includes a 0.5 to 3 microns thick, high carbon titanium carbonitride

initial layer (80% Ti, 19% C and 1% N), and the composition changes continuously with the content of combined carbon decreasing and nitrogen increasing until a 3 to 20 microns thick final or surface layer of titanium carbonitride with a high nitrogen content (77.5% Ti, 21.5% N and 1% C) is reached.

The disposable inserts coated in accordance with Examples I and II were subjected to machining tests under different cutting conditions and showed an increase in service life of approximately 10-30% compared with inserts coated with pure titanium nitride only. Because of the approximately 25 to 50% reduction in clearance face wear compared with the titanium nitride coated inserts, superior surface quality was displayed by the workpieces produced by the inserts of the present invention.

In thick wire drawing with steel wire (e.g., C60) at high drawing speeds, it was found that the drawing dies equipped with the combined coating of titanium carbide-titanium nitride has approximately 2.5 to 3 times longer service lives than uncoated dies whereas the drawing dies coated with titanium carbide only had approximately twice the service life of the uncoated dies.

EXAMPLE III

Clean cemented tungsten carbide cutting inserts or drawing dies with a 6% content of cobalt are heated in an oven at approximately 850° to 1200° C. in a gas mixture consisting of 0.6 volume % of titanium tetrachloride, 0.6% benzene, 60% argon and 39% hydrogen. The gas mixture reacts at the surface of the cemented carbide parts and titanium carbide is deposited. After 5 to 20 minutes, the supply of benzene and argon is discontinued, the charging of nitrogen is started and the proportions of hydrogen is increased. All of these adjustments are effected quickly so that no significant transition period occurs. The coating

is continued with the gas mixture, which now consists of 0.5% titanium tetrachloride, 69.5% hydrogen and 30% nitrogen, for another 20 to 60 minutes, with pure titanium nitride being deposited as the surface layer.

Metallographic study of the coating revealed that depending on the operating parameters, it is made up of a 0.5 to 2 microns thick initial titanium carbide layer contiguous with a 3 to 20 microns thick final layer of titanium nitride.

When subjected to machining tests and depending on the cutting conditions, disposable inserts equipped with this coating display an increase in service life of approximately 10-20% compared with disposable inserts coated with pure titanium nitride only.

EXAMPLE IV

Clean cemented carbide inserts (77% tungsten carbide, 10% titanium and tantalum carbides, with 13% cobalt) or tungsten carbide drawing dies of 12% cobalt content are heated in a furnace at approximately 850° to 1200° C. in a gas mixture consisting of titanium tetrachloride, benzene, argon and some hydrogen. The gas mixture reacts at the surface of the cemented carbide parts and titanium carbide is deposited. After approximately 5 to 15 minutes, the supply of benzene and argon is slowly diminished, nitrogen is introduced and the proportions of hydrogen and nitrogen are slowly increased during an interval of 10 to 30 minutes until benzene is no longer present. After 20 to 60 minutes, the proportion of nitrogen is slowly reduced and the charging of benzene and argon resumed in 10 to 30 minutes; finally coating is continued for another 1 to 10 minutes in a mixture now containing only titanium tetrachloride, hydrogen, argon and benzene. The steady gas mixtures are the same as in Example 3.

Metallographic examination of the coating showed that depending on the chosen conditions, the coating comprises a 0.5 to 3 microns thick titanium carbide initial layer in direct contact with the cemented carbide element, then the composition changes gradually and continuously with combined carbon decreasing and nitrogen increasing until a 3 to 20 microns thick layer of titanium nitride is reached; and overlying this are further layers of gradually decreasing combined nitrogen and increasing carbon content, and finally an approximate 0.1 to 0.5 micron thick layer of titanium carbide at the external surface.

Disposable inserts equipped with these coatings gave an important service life in milling applications of approximately 10-30% compared with inserts coated with pure titanium nitride or pure titanium carbide. Furthermore, the surface quality of the milled parts was superior to that of inserts coated with titanium nitride or carbide, because the inserts with the combined coating has less tendency to splintering of the cutting edges.

This invention is not restricted to the above-described embodiments which are intended for purposes of illustration. It may be used to advantage not only in all types of tools for machining and for drawing dies but also for other tools used in chipless forming. In principle, it is possible by means of the invention to increase the wear resistance of all parts which are subject to mechanical wear. Accordingly, the present invention should not be construed as limited in any particulars except as may be stated in the appended claims or required by the prior art.

I claim:

1. An article of manufacture comprising a hard metal or sintered carbide substrate and an adherent wear-resistant multilayer coating, the composition of said coating varying through its depth or thickness, wherein

the substrate has carbon disposed in a region adjacent the surface thereof, said region being formed by carburizing said substrate to increase its carbon content,

the coating layer adjacent the carburized surface comprises titanium carbide formed by reacting the carburized surface with a gaseous mixture comprising titanium halide, a hydrocarbon gas and hydrogen, and

the coating layer overlying the titanium carbide layer comprises titanium nitride formed by reacting the surface of the titanium carbide layer with a gaseous mixture comprising a nitrogen compound, titanium halide and hydrogen.

2. An article of manufacture as in claim 1 wherein the substrate is comprised of a cemented carbide.

3. An article of manufacture comprising:

(a) a hard metal or sintered carbide substrate; and

(b) a composite coating on at least one surface of said substrate, said composite coating including a layer of titanium carbide and a layer of titanium nitride overlying and adjacent said layer of titanium carbide.

4. The article of manufacture defined in claim 3 wherein said layer of titanium carbide is about 0.2 to 20 microns thick and said layer of titanium nitride is about 0.3 to 30 microns thick.

5. An article of manufacture as in claim 3 wherein the substrate is a cemented carbide.

6. In a tool having a wear surface comprised of a hard metal or a sintered carbide, a coating of titanium carbide covering said wear surface and a coating of titanium nitride covering said coating of titanium carbide.

7. A tool as in claim 6 wherein the wear surface is comprised of a cemented carbide.

8. A wear part of a tool having a portion which in use is exposed to wear through contact with an extraneous force, said wear part comprising:

(a) a cemented carbide substrate;

(b) a layer of a metal carbide overlying the cemented carbide; and

(c) a layer of metal nitride overlying the metal carbide, the metal of the metal carbide being selected from among chromium, molybdenum, tungsten, titanium, zirconium, hafnium, vanadium, niobium, and tantalum, and the metal of the metal nitride being selected from among chromium, titanium, zirconium, hafnium, vanadium, niodium [*sic*] and tantalum.

9. A wear part of a tool as in claim 8 wherein the cemented carbide is selected from the group consisting of (i) cemented tungsten carbide compositions containing about 5 to 30% of a binder metal of the iron group, or (ii) cemented carbides containing from about 60 to 90% of titanium carbide, with the balance comprising nickel or a nickel-molybdenum alloy binder.

10. A wear part of a tool as in claim 9 wherein the metal in the metal nitride and the metal in the metal carbide are each titanium.

11. A wear part of a tool as in claim 10 wherein the thicknesses of the individual titanium carbide and titanium nitride layers are from 0.2 to 20 microns and 0.3 to 30 microns respectively.

12. A wear part as in claim 11 in the form of an insert for a cutting tool.

13. A wear part as in claim 11 in the form of an insert for a die.

14. A wear part of a tool as in claim 9 wherein the metal in the metal nitride and the metal in the metal carbide are each at least 50% by weight titanium.

15. An article of manufacture comprising:
(a) A hard metal or sintered carbide substrate; and
(b) a composite coating on at least one surface of said substrate, said composite coating including a layer of titanium carbide, a transition layer containing titanium carbonitrides overlying said layer of titanium carbide and a layer of titanium nitride overlying said transition layer.

16. In a tool having a wear surface comprised of a hard metal or a sintered carbide, a coating of titanium carbide covering said wear surface, a transition layer containing titanium carbonitrides covering said coating of titanium carbide, and a coating of titanium nitride covering said transition layer.

17. A wear part of a tool having a portion which in use is exposed to wear through contact with an extraneous force, said wear part comprising:
(a) a cemented carbide substrate;
(b) a layer of a metal carbide overlying the cemented carbide;
(c) a layer of a metal carbonitride overlying the metal carbide; and
(d) a layer of a metal nitride overlying the metal carbonitride,
the metal of the metal carbide being selected from among chromium, molybdenum, tungsten, titanium, zirconium, hafnium, vanadium, niobium and tantalum, the metal of the metal carbonitride being selected from among chromium, molybdenum, tungsten, titanium, zirconium, hafnium, vanadium, niobium and tantalum, and the metal of the metal nitride being selected from among chromium,

titanium, zirconium, hafnium, vanadium, niobium and tantalum.

18. A wear part of a tool as in claim 17 wherein the cemented carbide is selected from the group consisting of (i) cemented tungsten carbide compositions containing about 5 to 30% of a binder metal of the iron group, or (ii) cemented carbides containing from about 60 to 90% of titanium carbide, with the balance comprising nickel or a nickel-molybdenum alloy binder, and the metal in the metal carbide, the metal in the metal carbonitride, and the metal in the metal nitride are each titanium.

19. A wear part of a tool having a portion which in use is exposed to wear through contact with an extraneous force, said wear part comprising:

(a) a cemented carbide substrate wherein the cemented carbide is selected from the group consisting of (i) cemented tungsten carbide compositions containing about 5 to 30% of a binder metal of the iron group, or (ii) cemented carbides containing from about 60 to 90% of titanium carbide, with the balance comprising nickel or a nickel-molybdenum alloy binder;

(b) a layer of titanium carbide having a thickness of from 0.2 to 20 microns overlaying the cemented carbide;

(c) an intermediate layer containing titanium, carbon and nitrogen overlaying the titanium carbide; and

(d) a layer of titanium nitride having a thickness of from 0.3 to 30 microns overlaying the intermediate layer,

the intermediate layer being carbon-rich, nitrogen-poor immediately adjacent the titanium carbide layer, and carbon-poor, nitrogen-rich immediately adjacent the titanium nitride layer.

APPENDIX H

UNITED STATES PATENT 4,162,338

United States Patent [19] [11] 4,162,338
Schintlmeister [45] Jul. 24, 1979

---

[54] COATED CEMENTED CARBIDE ELEMENTS AND THEIR MANUFACTURE

[75] Inventor: Wilfried Schintlmeister, Reutte, Austria
[73] Assignee: Schwarzkopf Development Corporation, New York, N.Y.

[21] Appl. No.: 875,071 [22] Filed: Feb. 3, 1978

Related U.S. Application Data

[60] Division of Ser. No. 571,695, Apr. 25, 1975, Pat. No. 4,101,703, which is a continuation of Ser. No. 329,128, Feb. 2, 1973, abandoned.

[30] Foreign Application Priority Data

Feb. 4, 1972 [AT] Austria 896/72
Jul. 21, 1972 [AT] Austria 6317/72

[51] Int. Cl.[2] B05D 1/36; B05D 3/10; B05D 7/14
[52] U.S. Cl. ..... 427/249; 148/6.3; 427/248 A; 427/248 B; 427/248 C; 427/248 E; 427/248 J
[58] Field of Search ..... 427/248 A, 248 B, 248 C, 427/248 J, 249, 248 E; 148/63

[56] References Cited

U.S. PATENT DOCUMENTS

3,642,522	2/1972	Gass et al.	427/249
3,656,995	4/1972	Reedy	427/249 X
3,684,585	8/1972	Stroup et al.	427/249 X
3,771,976	11/1973	Wakefield	427/249 X

Primary Examiner — James R. Hoffman
Attorney, Agent, or Firm — Morgan, Finnegan, Pine, Foley & Lee

[57] ABSTRACT

Cemented carbide elements with working faces bearing a thin multilayer or stratified coating of nonuniform composition of wear-resistant materials exhibit superior wear-resistance for improved performance and service life under severe service conditions as in the case of inserts for cutting tools and wire drawing dies. In one embodiment, an initial carbon-rich layer of titanium carbide or carbonitride coating material in direct contact with a cemented carbide part or insert underlies a middle or intermediate stratified transition zone made up of a series of parallel layers or strata of coating material wherein the content of carbon and nitrogen is not constant but varies with the stratum or location by depth in that zone with the material gradually changing to titanium compounds that are progressively lower in combined carbon content and richer in nitrogen than in the initial layer until the composition of the outermost stratum of the transition zone approximates that of the overlying surface layer of high nitrogen content (e.g., titanium nitride). The coating is formed by a gas deposition method wherein changes in the concentration of gaseous carbon and nitrogen compounds are used to control the formation of the various layers of different composition in the layered coating.

24 Claims, No Drawings

COATED CEMENTED CARBIDE ELEMENTS AND THEIR MANUFACTURE

This is a divisional of application Ser. No. 571,695 filed Apr. 25, 1975 (now U.S. Pat. No. 4,101,703), which is a continuation of application Ser. No. 329,128 filed Feb. 2, 1973 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with protective coatings for wear-resistant elements intended for severe operating

conditions and with methods of depositing such coatings on the wear-resistant substrates or inserts.

2. Prior Art

Cemented carbides, also known as sintered carbides, are solid and coherent masses made by pressing and sintering a mixture of powders of one or more metallic carbides and a much smaller amount of an iron group metal, such as cobalt, to serve as a binder metal. These carbides may be used as tools or inserts for machining, milling, blanking, and drawings operations; also as shaping dies, spinning dies, and for many other applications. Such tools are capable of performance beyond the limits of high speed steels and in many cases are suitable for use on very hard abrasive materials and on tough alloys. Cemented carbides are widely used for structural parts and tools subject to intense wear or other service loads that require high compressive strength. Suitable carbides for such purposes include the carbides of tungsten, titanium, tantalum, columbium, molybdenum, vanadium, chromium, zirconium, and hafnium.

Cemented carbides because of their unique strength and hardness are frequently subjected to conditions of intense wear. The manner and rate of wear depends very largely on the use and service conditions of the cemented carbide part. Wear is frequently caused by mechanical abrasion which can be greatly intensified by diffusion processes when operating at elevated temperatures. Corrosion is also a cause in the wear of such parts, for example, when cemented carbide is used in corrosive media or when oxidation in the air takes place at elevated temperatures. When cemented carbides are used for shaping of other parts, either by machining and nonchipping shaping operations or by other processes, the cemented carbide parts are not only subjected to heavy mechanical

stresses but there is frequently also intense heating which greatly accelerates the wear.

In the machining of long-chipping and short-chipping materials, as for example, steel or cast iron, respectively, wear on the cutting edge can occur as a result of cratering of the rake face and abrasion of the clearance face. Furthermore, the chips can adhere or weld onto the cutting edge of the part and cause chipping or splintering of the edge. In interrupted cuts, crack formation may be caused by rapid temperature changes and splintering can occur from heavy impacts.

It has now been discovered that wear-resistant stratified coatings composed of a number of layers of certain different compositions provide a number of significantly improved results of an unpredictable nature as described hereinafter, particularly when these coatings are employed as protective wear-resistant coatings on cemented carbide substrates and other hard material bases. The coated articles have many uses for metal working and other purposes that involve exposure to mechanical wear and abrasion.

SUMMARY OF THE INVENTION

The present invention relates to a hard water [*sic*]-resistant multilayer coating of nonuniform composition in adjoining layers and wherein said coating contains at least two different wear-resistant materials and includes at least two elements of the group consisting of carbon, nitrogen, boron and silicon in chemical combinations with titanium. It also encompasses articles with such coatings on hard material bases or substrates of the type described hereinafter, and especially cemented carbides substrates having an adherent coating that contains at least two different wear-resistant materials and includes carbon and nitrogen in chemical combination with titanium.

This invention also encompasses a method of making the aforesaid articles by deposition onto substrates from reactive gaseous mixtures under controlled reaction conditions, including the composition of the gaseous mixtures.

Other aspects of the invention involve one or more of such features as the structure of the multilayer (i.e., more than one layer) article and the thickness and disposition or location of its layers, especially carbon-rich layers composed of material of a substantial or high carbon content and a lower nitrogen content, as well as nitrogen-rich layers of material containing less carbon than nitrogen.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The coated articles of the invention may employ as a base or substrate any hard solid material to which the coatings will adhere. These hard materials are generally hard metals or alloys thereof, including metal-like alloys, compositions or materials. Thus, the substrates may be cermets and like products of powder metallurgy, as well as hard metal carbides and/or nitrides, etc. and alloys, such as cobalt-chromium-tungsten, superalloys and other alloys employed in high speed cutting tools. In general, sintered materials are preferred as substrates, especially the wear-resistant cemented carbides. Among the many suitable base or substrate materials, cemented tungsten carbide compositions containing about 5-30% of a binder metal of the iron group (cobalt, iron, and/or nickel) have been used with excellent results, and up to a total of 40% of the tungsten carbide content may be replaced by one or more other carbides, including those of titanium, tantalum, niobium, vanadium or chromium. Cemented carbides containing from 60-90% titanium carbide with the balance being nickel or a nickel-molybdenum alloy binder

are also used and up to half of this titanium carbide may be replaced by titanium nitride.

A coating of the present invention is characterized by a multilayer structure, often so thin that the total thickness of the coating is less than 10 or 20 microns, as well as the fact that its chemical composition is not uniform or homogeneous although its physical appearance is typically homogeneous with no strata visible even under a microscope. These coatings are made up of two or more layers, and at least two of the layers are of different composition in respect to having either different chemical components or different proportions of the same components or elements. The principal constituents of the coatings are metal compounds of at least two nonmetals of the group consisting of carbon, nitrogen, boron and silicon, of which carbon and nitrogen are generally preferred. But also compounds of nonmetals, such as boron carbide, boron nitride and silicon carbide, can be used. Titanium may be utilized as the sole metallic component of such compounds; also it is contemplated that it may be associated with considerable amounts of compounds of one or more other metals in Groups III, IV, V and VI of the Periodic Table of Elements that have atomic numbers in the range of 21 to 74. Thus, one may also employ compounds of one or more of such metals as chromium, molybdenum, tungsten, scandium, yttrium, lanthanum, zirconium, hafnium, vanadium, niobium and tantalum, usually in lesser total amount so that the titanium constitutes a major portion or more that [*sic*, than] 50% of the total weight of the chemically combined metals in the coatings. In some cases it may be also useful to substitute more than 50% of the titanium. If coatings having particularly great ductility are required, then additions of iron, cobalt, or nickel, or molybdenum, or mixtures thereof up to about 20% of the total coating weight are advantageous. While the specific description hereinafter is directed entirely at coatings

composed of titanium compounds and their deposition for the purposes of a full and detailed disclosure of materials that have provided greatly improved results, such description is generally applicable to coatings which also contain the compounds of the aforementioned other metals and nonmetals.

In respect to the contents of nonmetals in the titanium compounds in the coatings of this invention, a nitrogen or carbon content of more than 14% by weight is regarded as a high nitrogen or high carbon content. Amounts of these elements below 6% are considered low contents, and the intermediate range of 6-14% may be called an average or medium content of carbon or nitrogen. On the other hand, the expressions "carbon-rich" and "nitrogen-rich" herein are intended to denote coating deposits wherein carbon or nitrogen, respectively, constitutes a major proportion of the total weight of the combined nonmetals in the particular deposits and also to denote gaseous mixtures containing enough carbon-containing or nitrogen-containing gas material to produce such solid deposits. In general, this means that a solid deposit has a carbon or nitrogen concentration, respectively, that is either a high content or in the upper half of the intermediate content range, say above 10%.

In general, the chemical compositions of each of the various layers or strata are substantially uniform in their planar dimensions, that is across the entire width and length of their areas, by reason of the manner of their deposition from the vapor state onto solid bases or substrates as described hereinafter; instead, the desired and significant differences in composition occur through the depth or thickness of the coating, and the composition of one principal layer is different from the adjoining overlying or underlying layer; and this difference in composition may be slight and progressive in gradations through a

transition zone having many ultra-thin strata in some instances or a more pronounced change in other cases.

The arrangement, thickness and composition of the individual layers will depend upon the surface conditions of the wear part. For instance, these may consist of several different layers, namely pure titanium carbide, titanium carbonitrides of medium to high carbon content, pure titanium nitride or titanium carbonitrides with a high nitrogen content. In some cases, it may be advantageous to have five or more layers while in other cases, two principal layers may be sufficient, for example, a carbon-rich layer and a nitrogen-rich layer of titanium compounds. The individual layers can be either contiguous or there may be an intermediate stratified transition zone wherein the intermediate layers or strata have variable carbon and nitrogen contents; that is, the combined carbon content is decreasing and the combined nitrogen content increasing in one direction through the thickness of that zone (e.g., away from the substrate and toward the exterior surface of the composite coating), and the carbon is increasing and nitrogen decreasing in the other direction (e.g., toward the substrate). Such changes in composition may be essentially continuous or very gradual in such a transition zone wherein the composition is changed from a composition similar to that of a principal layer on one side of the zone to a composition similar to that of a different principal layer on the other side of the zone. On the other hand, the change in composition may be very marked as at the single interface of two contiguous carbon-rich and nitrogen-rich coating layers.

The thickness of a transitional carbonitride layer or zone may be about 0.1 to 10 microns. The individual or principal layers of titanium nitride and titanium carbonitride having medium to high nitrogen content, are usually present in thickness of about 0.3 to 30 microns. The indi-

vidual or principal layers of titanium carbide and titanium carbonitride having a low nitrogen content are usually present in thicknesses of 0.2 to 20 microns.

In many cases, it has been found advantageous to have a layer structure in which the layer or stratum with the maximum carbon content is located close to the base or substrate surface and remote from the external surface of the coating, whereas the layer or stratum of maximum nitrogen content is located close to the surface of the coating, and remote from the substrate. For example, the layer near the base may consist of titanium carbide or a titanium carbonitride and the layer near the surface of the coating of titanium nitride. The coating can be formed in such a manner that a pure titanium carbide layer is joined to a pure titanium nitride layer by means of a series of carbonitride layers in a transition zone that provides a gradual and continuous change in composition from carbide to nitride.

The formation of the coating layers in accordance with the present invention can be most simply carried out by use of a gas phase deposition. However, other well known methods such as plasma spraying, sputtering, or pack cementation have also been found useful.

Gas phase deposition has the particular advantage that the layer composition can be readily controlled by regulation of the composition, the pressure and temperature of the gas phase. The composition of the gas phase can easily be adjusted by addition of suitable gaseous compounds. Furthermore, the mixing ratio of the gas may also be varied during the deposition process in a simple manner which causes a corresponding change in the deposited coating composition. The cemented carbide parts may be cleaned by conventional techniques prior to applying the coating material. Surface carburization of the cemented carbide substrates may also be carried out where the car-

bon content of the cemented carbide is too low for effective coating with the hard materials of this invention.

Atmospheric pressure may be employed for the gas deposition of all the coating materials as in the examples that follow, but it is also contemplated that it may be desirable to employ higher or lower pressures in some instances. For example, it may be advantageous to employ subatmospheric pressures for depositing coatings of titanium carbide, and it is also contemplated that titanium nitride deposits may be formed with a gaseous mixture at superatmospheric pressures. Suitable operating temperatures for the preferred titanium compounds of carbon and nitrogen are in the 700° to 1200° C. range.

The gas mixture is varied depending upon the composition of the layer desired to be deposited. Generally, in order to form a pure titanium nitride layer, the gas mixture comprises a titanium halide, for example, titanium tetrachloride; nitrogen or gaseous nitrogen compounds such as ammonia, and similar nitrogen compounds. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof.

In order to form titanium carbonitride layers, a gas mixture preferably comprises a titanium halide, a hydrocarbon gas, and nitrogen or a gaseous nitrogen compound, such as, aniline, pyridine, aliphatic and aromatic amines and similar organic nitrogen compounds. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof.

In order to form a pure titanium carbide layer, the gas mixture may comprise a titanium halide, and hydrocarbon gas. The gas mixture may also contain inert gases, or hydrogen, or a mixture thereof. Other sources of carbon for the process are the vapors of organic halides of either the aliphatic or aromatic type.

According to the present invention, there is provided a new coating for cemented carbide parts which reduces abrasion and cratering of the surfaces of the cemented carbide tool inserts to a surprising and outstanding degree. This is in marked contrast with results that have been obtained with tool inserts bearing a coating of uniform composition. For instance, special cutting disposable inserts and tips made of cemented carbides for machining parts have recently been developed, and these have a wear-resistant surface coating of titanium carbide. Such disposable cutting inserts, e.g., coated with titanium carbide, generally have had two to three times the service life of similar uncoated disposable tips when used under comparable machining conditions. However, their service life is limited by the cratering type of wear although the clearance face wear is relatively slight.

It has been proposed in the U.S. Pat. No. 3,717,496 to coat cemented carbide inserts with titanium nitride or titanium carbonitrides in order to reduce wear. In practice it was found that titanium carbide produces better protection for the clearance face, whereas titanium nitride provides higher resistance to cratering, but the clearance face wear is 2 or 3 times greater than with a comparable insert coated with titanium carbide. Accordingly, in the case of titanium nitride coatings, the great clearance face wear frequently causes failure of the inserts before marked cratering has occurred; hence, the improved cratering resistance could not even be utilized.

It has now been discovered that the coatings of the present invention which may consist of different or alternating layers rich in titanium combined with nitrogen and carbon, respectively, impart a much greater wear-resistance in cutting tools than a uniform coating composition of either alone. While the cause for this is not completely understood, this phenomenon is probably due to

the fact that each of the layers react differently to the different types of wear. As previously mentioned, the clearance face wear in cutting tools is predominantly due to abrasion, while the cratering wear is primarily due to diffusion. If part of a tool coated according to this invention is subjected to one of such types of wear, it is thought that if the uppermost layer contains a composition with little resistance to this type of wear, it will be rapidly abraded and thus expose the next layer having a different composition which is more likely to be highly resistant to this type of wear. Moreover, the combination of the different layers provides surprising and improved results as mentioned hereinafter.

An important advantage of the combination of layers of the new coatings is that they have a less pronounced epitaxial structure and a finer grain structure, and this reduces possibility of cracking and chipping of the layers.

Additional advantages are found when the new coated tool elements are subjected to interrupted cuts, particularly in milling, for they display greater resistance to cyclical temperature changes and to impact effects.

The structure of the coating layers of the present invention is not only of significance for cutting tools, but is equally advantageous for tools used for non-chipping, shaping operations, e.g., for drawing, swaging, or forging.

When drawing thick steel wire using drawing dies coated with titanium carbide alone it has been found that the titanium carbide is highly resistant to the large tensile forces exerted on the surface of the drawing die bore; however, galling of the wire was observed relatively early. The formation of undesirable grooves in the wire was found to be due to peeling of the titanium carbide coating.

When drawing dies were equipped with the combined titanium carbide-titanium [*sic*, titanium nitride] coating of this invention, there appeared to be a substantial reduction in the coefficient of friction, for the drawing force was rendered [*sic*]; consequently the service life was increased compared with the comparable drawing dies having only a pure titanium carbide coating. This reduction of the drawing force also makes it possible to effect larger reductions in a single pass.

The following examples illustrate the practice of the invention.

EXAMPLE I

Cemented carbide plates (84% tungsten carbide, 10% titanium and tantalum carbides with 6% cobalt as a binder metal) or drawing dies (tungsten carbide containing 6% cobalt as a binder metal) which are to be coated are first cleaned and then carburized in order to enrich the surface with carbon. The cemented carbide parts are then annealed at 850° to 1200° C. in a gas mixture consisting of 92.3 volume % of hydrogen, 0.4% titanium tetrachloride, 7% methane and 0.3% nitrogen. The gas mixture reacts at the surface of the cemented carbide part and forms an initial titanium carbonitride deposit with a high carbon content. After 5 to 20 minutes, the flow of methane is slowly reduced and that of the nitrogen increased over a period of 10 to 40 minutes. After this operation, the parts are coated for 20 to 60 minutes in a gas mixture consisting of 0.5% titanium tetrachloride, 69.5% hydrogen and 30% nitrogen, which yields a final layer of pure titanium nitride.

Metallographic examination of the coatings showed that, depending upon the process parameters (temperature, time and gas composition), the coatings comprise a 0.5 to 3 microns thick initial layer of titanium carbonitride

of high carbon content (80% titanium, 18% carbon and 2% nitrogen) in contact with the carburized cemented carbide substrate, and the composition of the deposited material changes gradually to provide a 3 to 20 microns thick surface layer of titanium nitride. Since titanium carbide and titanium nitride are miscible in any proportions, sharp boundaries between the individual layers in the coating cannot be observed.

EXAMPLE II

Cemented carbide tips (71% tungsten carbide, 20% titanium and tantalum carbides with 9% cobalt) or drawing dies (tungsten carbide containing 9% cobalt binder) to be coated are first cleaned and may be subsequently carburized in order to enrich the surface with carbon. The parts are then annealed at 850° to 1200° C. in a gas mixture consisting of 0.4 volume % of titanium tetrachloride, 10% methane, 0.2% nitrogen and the remainder of hydrogen. The gas mixture reacts at the surface of the cemented carbide parts resulting in the deposition of a titanium carbonitride of high carbon content. After 5 to 20 minutes, the proportion of methane is slowly reduced, while that of nitrogen is increased during a transition deposition period of 30 to 60 minutes. The parts are further coated in a gas mixture consisting of 0.4% by volume of titanium tetrachloride, 1.2% methane, 74% hydrogen and 25% nitrogen, with the nitrogen content now higher than the methane content, for another 20 to 60 minutes, with the result, that a titanium carbonitride layer of high nitrogen content is now deposited. Atmospheric pressure is employed in all of the foregoing treatments and in all other detailed examples herein.

Metallographic examination of the coatings showed that, depending on the process conditions, each includes a 0.5 to 3 microns thick, high carbon titanium carbonitride

initial layer (80% Ti, 19% C and 1% N), and the composition changes continuously with the content of combined carbon decreasing and nitrogen increasing until a 3 to 20 microns thick final or surface layer of titanium carbonitride with a high nitrogen content (77.5% Ti, 21.5% N and 1% C) is reached.

The disposable inserts coated in accordance with Examples I and II were subjected to machining tests under different cutting conditions and showed an increase in service life of approximately 10-30% compared with inserts coated with pure titanium nitride only. Because of the approximately 25 to 50% reduction in clearance face wear compared with the titanium nitride coated inserts, superior surface quality was displayed by the workpiece produced by the inserts of the present invention.

In thick wire drawing with steel wire (e.g., C60) at high drawing speeds, it was found that the drawing dies equipped with the combined coating of titanium carbide-titanium nitride has approximately 2.5 to 3 times longer service lives than uncoated dies whereas the drawing dies coated with titanium carbide only had approximately twice the service life of the uncoated dies.

EXAMPLE III

Clean cemented tungsten carbide cutting inserts or drawing dies with a 6% content of cobalt are heated in an oven at approximately 850° to 1200° C. in a gas mixture consisting of 0.6 volume % of titanium tetrachloride, 0.6% benzene, 60% argon and 39% hydrogen. The gas mixture reacts at the surface of the cemented carbide parts and titanium carbide is deposited. After 5 to 20 minutes, the supply of benzene and argon is discontinued, the charging of nitrogen is started and the proportions of hydrogen is increased. All of these adjustments are effected quickly so that no significant transition period occurs. The coating

is continued with the gas mixture, which now consists of 0.5% titanium tetrachloride, 69.5% hydrogen and 30% nitrogen, for another 20 to 60 minutes, with pure titanium nitride being deposited as the surface layer.

Metallographic study of the coating revealed that depending on the operating parameters, it is made up of a 0.5 to 2 microns thick initial titanium carbide layer contiguous with a 3 to 20 microns thick final layer of titanium nitride.

When subjected to machining tests and depending on the cutting conditions, disposable inserts equipped with this coating display an increase in service life of approximately 10-20% compared with disposable inserts coated with pure titanium nitride only.

EXAMPLE IV

Clean cemented carbide inserts (77% tungsten carbide, 10% titanium and tantalum carbides, with 13% cobalt) or tungsten carbide drawing dies of 12% cobalt content are heated in a furnace at approximately 850° to 1200° C. in a gas mixture consisting of titanium tetrachloride, benzene, argon and some hydrogen. The gas mixture reacts at the surface of the cemented carbide parts and titanium carbide is deposited. After approximately 5 to 15 minutes, the supply of benzene and argon is slowly diminished, nitrogen is introduced and the proportions of hydrogen and nitrogen are slowly increased during an interval of 10 to 30 minutes until benzene is no longer present. After 20 to 60 minutes, the proportion of nitrogen is slowly reduced and the charging of benzene and argon resumed in 10 to 30 minutes; finally coating is continued for another 1 to 10 minutes in a mixture now containing only titanium tetrachloride, hydrogen, argon and benzene. The steady gas mixtures are the same as in Example 3.

Metallographic examination of the coating showed that depending on the chosen conditions, the coating comprises a 0.5 to 3 microns thick titanium carbide initial layer in direct contact with the cemented carbide element, then the composition changes gradually and continuously with combined carbon decreasing and nitrogen increasing until a 3 to 20 microns thick layer of titanium nitride is reached; and overlying this are further layers of gradually decreasing combined nitrogen and increasing carbon content, and finally an approximate 0.1 to 0.5 micron thick layer of titanium carbide at the external surface.

Disposable inserts equipped with these coatings gave an improved service life in milling applications of approximately 10-30% compared with inserts coated with pure titanium nitride or pure titanium carbide. Furthermore, the surface quality of the milled parts was superior to that of inserts coated with titanium nitride or carbide, because the inserts with the combined coating have less tendency to splintering of the cutting edges.

This invention is not restricted to the above-described embodiments which are intended for purposes of illustration. It may be used to advantage not only in all types of tools for machining and for drawing dies but also for other tools used in chipless forming. In principle, it is possible by means of the invention to increase the wear resistance of all parts which are subject to mechanical wear. Accordingly, the present invention should not be construed as limited in any particulars except as may be stated in the appended claims or required by the prior art.

I claim:

1. A method of producing an article of manufacture comprising a hard metal or cemented carbide substrate and an adherent wear-resistant coating, the composition of said coating varying through its depth and thickness,

from essentially pure titanium carbide closest to the substrate to essentially pure titanium nitride furthest from the substrate, comprising the steps of:

(a) reacting the surface of said substrate with a gaseous mixture comprising a titanium halide, a hydrocarbon gas, and hydrogen to form a titanium carbide layer adjacent the surface of said substrate; and

(b) reacting the surface of the titanium carbide layer with a gaseous mixture comprising a titanium halide, a nitrogen-containing gas, and hydrogen to form a layer comprising titanium nitride overlying the titanium carbide layer.

2. A method of producing an article of manufacture comprising a hard metal or cemented carbide substrate and an adherent wear-resistant coating, the composition of said coating varying through its depth and thickness, from essentially pure titanium carbide closest to the substrate through an intermediate titanium carbonitride zone to essentially pure titanium nitride furthest from the substrate, comprising the steps of:

(a) reacting the surface of said substrate with a gaseous mixture consisting essentially of a titanium halide, a hydrocarbon gas, and hydrogen to form a titanium carbide coating layer adjacent to the surface of said substrate;

(b) reacting the surface of the titanium carbide layer with a gaseous mixture consisting essentially of a titanium halide, a hydrocarbon gas, a nitrogen-containing gas, and hydrogen to form a titanium carbonitride coating layer overlying the titanium carbide layer; and

(c) reacting the surface of the titanium carbonitride layer with a gaseous mixture consisting essentially of a titanium halide, a nitrogen-containing gas,

and hydrogen to form a titanium nitride coating layer overlying the titanium carbonitride layer.

3. A method of producing an article of manufacture comprising a cemented carbide substrate bearing an adherent wear-resistant coating, the composition of said coating varying through its depth and thickness from titanium carbide rich, titanium nitride poor closest to the substrate to titanium nitride rich, titanium carbide poor furthest from the substrate, said method comprising depositing titanium compounds from gaseous mixtures comprising a gaseous titanium compound, a hydrocarbon gas and a nitrogen-containing gas, regulating the quantities of hydrocarbon gas and nitrogen-containing gas present in the mixture at any given time to provide first a hydrocarbon gas rich, nitrogen gas poor mixture and finally a hydrocarbon gas poor, nitrogen gas rich mixture, to thereby deposit from the vapor phase an essentially pure titanium carbide coating layer closest to said substrate, an intermediate coating layer of titanium carbonitrites and an essentially pure coating layer of titanium nitride furthest from said substrate.

4. A method according to claim 3 at least one layer of a coating material of the group consisting of a titanium carbide and a titanium carbonitride is deposited from a carbon-rich gaseous mixture subatmospheric pressure, and at least one layer of a coating material of the group consisting of a titanium nitride and a titanium carbonitride is deposited under superatmospheric pressure from a nitrogen-rich gaseous mixture of not more than low carbon content.

5. A method according to claim 3 in which said gaseous mixtures contain in inert gas or hydrogen or mixtures thereof.

6. A method according to claim 3 in which the surface of said cemented substrate is carburized prior to the deposition of said coating material.

7. The method of claim 1 wherein the surface of said substrate is first carburized to dispose carbon in a region adjacent to the surface of said substrate.

8. The method of claim 2 wherein the surface of said substrate is first carburized to dispose carbon in a region adjacent to the surface of said substrate.

9. A method as in claim 1 wherein the article of manufacture is in the form of a coating* insert for a tool.

10. A method as in claim 9 wherein the substrate is a cemented carbide.

11. A method as in any of claims 1, 2, 3 and 10 in which the nitrogen-containing gas is nitrogen.

12. A method as in claim 2 wherein the article of manufacture is in the form of a coating* insert for a tool.

13. A method as in claim 11 wherein the adherent wear-resistant coating is applied so as to form the wear surface of a tool

14. A method as in claim 2 wherein the adherent wear-resistant coating is applied so as to form the wear surface of a tool.

15. A method as in claim 2 wherein the adherent wear-resistant coating is applied so as to form the wear surface of a die.

16. A method for applying a coating to a cemented carbide substrate, said substrate being in the shape of an insert for use as the cutting edge of a tool, consisting essentially of heating the substrate while it is exposed to a first vapor phase consisting essentially of a titanium compound and a hydrocarbon, for a period and at a tempera-

---

* *Cf.* Certificate of Correction, page H-22 *infra*.

ture sufficient to deposit from said vapor phase a coating layer of titanium carbide, and thereafter, substituting a nitrogen-containing gas for said hydrocarbon to form a second vapor phase, and exposing the substrate to the resulting second vapor phase for a period and at a temperature sufficient to deposit therefrom a coating layer of titanium nitride over said titanium carbide coating layer, the combination of the coatings resulting in a composite insert exhibiting enhanced resistance to both crater wear and clearance face wear.

17. A method as in claim 16 wherein the titanium compound is titanium tetrachloride, the hydrocarbon is methane, and the nitrogen-containing gas is nitrogen.

18. A method as in claim 17, wherein each vapor phase also contains hydrogen and argon.

19. A method as in claim 16 wherein the titanium compound is titanium tetrachloride.

20. A method as in claim 16 wherein, after deposition of the coating layer of titanium carbide over the substrate, the composition of the first vapor phase is changed to form an intermediate vapor phase by addition of a nitrogen-containing gas thereto, for a period and at a temperature sufficient to deposit titanium carbonitride coating over said titanium carbide coating, and thereafter removing the said hydrocarbon to form the second vapor phase, which then deposits the titanium nitride coating over the titanium carbonitride coating.

21. A method as in claim 20 wherein the titanium compound is titanium tetrachloride, the hydrocarbon is methane, and the nitrogen-containing gas is nitrogen.

22. A method as in claim 21 wherein each vapor phase also contains hydrogen and argon.

23. A method as in claim 20 or 21 wherein, after deposition of the titanium carbide coating layer, and before deposition of the titanium nitride coating layer, the proportions of hydrocarbon and of nitrogen-containing gas contained in the intermediate vapor phase are gradually adjusted from hydrocarbon rich to nitrogen rich so as to deposit a titanium carbonitride coating layer that varies in composition from carbon rich adjacent to the titanium carbide coating layer to nitrogen rich adjacent to the titanium nitride coating layer.

24. A method as in claim 17 or 21 in which the first vapor phase is maintained at a subatmospheric pressure during deposition of the titanium carbide coating layer.

UNITED STATES PATENT AND TRADEMARK OFFICE
– CERTIFICATE OF CORRECTION –

PATENT NO.: 4,162,338
DATED: August 9, 1979
INVENTOR(S): Wilfried Schintlmeister

It is certified that error appears in the above-entitled patent and that said Letters Patent are hereby corrected as shown below:

In *Column 10, line 21* and in *Column 10, line 27,* "coating" should be changed to -- cutting --

[SEAL]

Signed and Sealed this
Fifth Day of February 1980

Attest:

SIDNEY A. DIAMOND
Commissioner of Patents
and Trademarks

Attesting Officer

APPENDIX I

DECISION ON PETITION

(United States Department of Commerce —
Patent and Trademark Office)

(Filed February 27, 1985)

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

Group 150 Paper No. 7
Ex parte Schwarzkopf Development Corp
Reexam No. 90/000,655
Filed: 10/24/84
For: Coated Cemented Carbide Elements

This application for reexamination of U.S. Patent 4,101,703 has been forwarded to the Director of Patent Examining Group 150 for consideration of a petition filed under 37 CFR 1.181(b) and 37 CFR 1.515(c).

The petition is timely and is properly before the Director of Group 150 for consideration. SEE MPEP 1002. 02(c)(14).

Petitioner raises five (5) issues (a-e on page 8 of the petition) why he feels the decision denying the request for reexamination should be overturned and reexamination granted. These five (5) issues will be answered serially.

Issue (a). Alleges that using the rationale set forth in the decision of In re Yamamoto, 740 F.2d 1569 (fed. Cir. 1984) claims 3-6 can be interpreted to include an intervening layer between the cemented carbide substrate and the titanium carbide layer. Claim 3 calls for an

article comprising said substrate and a composite coating on at least one surface of said substrate. If in fact there is an intervening layer the titanium carbide would not be *on* the substrate but on the intervening layer. Claim 6 calls for a wear surface comprised of a hard metal or sintered carbide, a coating of titanium carbide covering said wear surface and a coating of titanium article covering said coating of titanium carbide. This claim calls for the titanium to *cover* the wear surface — not any other surface or layer.

In as much as petitioner's entire request for reexamination rests on his interpretation of the claim language, all the other arguments are moot. The prior art was considered in the context of the claims requiring the titanium carbide layer to be in contact with the wear surface and said claims have been found patentable over the prior art of record.

Issue (b). In view of petitioner's viewpoint being considered self serving with respect to the interpretation of the claim language it is not convincing in arriving at his conclusion.

Issue (c). The newly cited art is seen to be cumulative with respect to the art considered during prosecution and during interference proceedings on the instant patent.

Issues (d) and (e). Petitioner appears to urge that the argument raised by Ohlsson during the interference are different and, moreover, Ohlsson's arguments were not considered on their merits. Whether the issues raised by Ohlsson are the same or different is irrelevant since consideration was given to petitioner's request on its own merits and rejected. The fact that a written discussion of the art cited by Ohlsson was not made does not mean Ohlsson's arguments were not considered. What it in

fact means is that the primary examiner considered Ohlsson's arguments and the prior art cited and concluded the interference claims were patentable. In view of this conclusion the primary examiner declined to dissolve the interference on the grounds that the count(s) were unpatentable to patentee of the instant case and directed the interference to proceed. Petitioner interprets a failure to take additional action to dissolve as a failure to consider the arguments raised by Ohlsson. This is not the case.

In view of the foregoing, the decision of the primary examiner to deny the request for reexamination is deemed proper and not an abuse of discretion requiring supervisory intervention here.

The petition is *DENIED*.

This decision is final and nonappealable 37 CFR 1.515(c). No further communication on this matter will be acknowledged or considered.

This application will be forwarded to Finance Branch for processing petitioner's refund of $1,200 in accordance with 35 U.S.C. 303(c) and 37 CFR 1.26(c).

/s/ James O. Thomas, Jr.,
Director
Patent Examining Group 150
High Polymer Chemistry, Plastics, Coating
Photography, Stock Materials and Compositions

Morgan, Finnegan, Pine, Foley & Lee
345 Park Ave., New York, N.Y. 10022
Leydig, Voit, Osann, Mayer & Holt, Ltd.
1 IBM Plaza, Ste. 4600, Chicago, Ill. 60611

APPENDIX J

AFFIDAVIT OF ANDREW E. PIERCE

(United States District Court —
Southern District of New York)

(Dated February 21, 1985)

(SCHWARZKOPF DEVELOPMENT CORPORATION, Plaintiff, vs. TI-COATING, INC., Defendant – Case No. 83 Civ. 9042 (LBS))

AFFIDAVIT

County of Oakland
State of Michigan — SS

Andrew E. Pierce, the undersigned, being duly sworn deposes and says:

1. That he is a member of the bar of the District of Columbia, a graduate of Boston University, Boston, Massachusetts, with a Bachelor of Arts Degree in Biology, and a graduate of Suffolk University Law School, Boston, Massachusetts, with a Juris Doctor Degree; that from 1952 to 1969 he was employed as a research chemist or as a quality control chemist having worked during this period about ten years for the Borden Chemical Company as a research chemist, and about three years for the Chicopee Manufacturing Corporation, a division of Johnson and Johnson, as a textile research chemist, with the remainder of his experience as a chemist involved in positions as a quality control chemist; that subsequent to his graduation from Suffolk University Law School in 1968 and starting in 1969 until the present he has been employed as a patent attorney, having worked in this capacity for the Hooker Chemical Company for about five years, the BASF Wyan-

dotte Corporation for about seven years, the American Optical Corporation for about one year, and for the remainder of the time during this period having worked as a private practitioner of patent law; that over the past year he has served as an instructor in the evening division of the Oakland Community College having taught courses in patent law for inventors and business men, and

2. That the Ti-Coating, Inc. process for the production of coated cemented carbide elements according to information obtained from Mr. Al Plavel, an employee of Ti-Coating, Inc., is as follows:

A cemented carbide also known as a sintered carbide is used as a substrate onto which wear-resistant coatings are applied; that the substrate can be a so-called "straight grade" sintered carbide containing approximately 70% or more by weight of tungsten carbide and about 4 to 30% by weight of cobalt as a binder with the common grades of sintered carbide substrates containing about 6% by weight cobalt and the balance tungsten carbide; that the substrate is also utilized in a so-called "complex grade" of tungsten carbide alloy which can contain about 70% or more by weight of tungsten carbide, about 4 to about 15% by weight of cobalt as a binder and lesser amounts of tantalum carbide, titanium carbide, and niobium carbide; that in the Ti-Coating Incorporated process, a first coating layer consisting essentially of titanium nitride is applied to the sintered tungsten carbide substrate followed by a second or overlying layer of titanium carbide which is overlaid with a third layer of titanium carbonitride and a subsequently applied top or fourth layer of titanium nitride; that these coating layers are applied to the substrate without any attempt to carburize or increase the concentration of carbon on the surface of the substrate by a specific step in the coating process; that in accordance with the information obtained from Mr. Al Plavel of

Ti-Coating Incorporated, the sintered carbides to be coated which are obtained from customers of Ti-Coating have not been previously carburized; that these coatings are applied in accordance with a procedure involving flowing gases into a reactor and exhausting gases from the reactor on a continuous basis and in accordance with the following steps:

(a) the reactor is heated to 1000° C under a hydrogen atmosphere,

(b) nitrogen is thereafter introduced together with titanium tetrachloride and the sintered tungsten carbide is coated for a period of 30 minutes to form a layer of titanium nitride having a thickness of about 0.5 to about 1 micron, thereafter the flow of gas is shut off,

(c) the temperature is increased to 1050° C over a 15 minute period and thereafter methane and titanium tetrachloride are flowed into the reactor for a period of one hour and fifteen minutes, thereafter

(d) the temperature is reduced to 1000° C over a 15 minute period,

(e) nitrogen is introduced at a temperature of 1000° C in addition to continuing the flow of methane and titanium tetrachloride and the sintered carbides are coated for a period of 45 minutes to form a coating layer of titanium carbonitride over the layer of titanium carbide previously formed,

(f) the methane flow is shut off and the flow of hydrogen is started so that a combination of nitrogen, hydrogen and titanium tetrachloride are flowed into the reactor at a temperature of 1000° C over a period of 45 minutes to form a coating of titanium nitride over the previously formed layer of titanium carbonitride,

(g) the flow of gases is stopped with the exception of hydrogen and the reactor cooled over a period of 6 to 8 hours;

That the percent by volume of the gaseous mixtures used to form the various layers on the sintered carbide substrate is as follows:

(a) the first layer consisting essentially of titanium nitride is formed by exposing the sintered carbide at a temperature of 1000° to a gas mixture in percent by volume as follows:

hydrogen – 67%
nitrogen – 30%
titanium tetrachloride – 3%

(b) the second layer consisting essentially of titanium carbide is formed by exposing the previously coated substrate to the following percent by volume gas composition at a temperature of 1050° C:

methane – 3.8%
hydrogen – 90.2%
titanium tetrachloride – 3%

(c) the third layer consisting essentially of titanium carbonitride is formed over the titanium carbide layer by exposing the previously coated substrate at a temperature of 1000° C to the following gas composition expressed in percent by volume:

titanium tetrachloride – 3%
hydrogen – 69.6%
nitrogen – 25.0%
methane – 2.4%

(d) The fourth layer consisting essentially of titanium nitride is formed over the layer of titanium carbonitride by exposing the coated substrate at a temperature of 1000° C to the following gas composition expressed in percent by volume:

titanium tetrachloride – 3%
nitrogen – 30%
hydrogen – 67%

That it is understood from conversations with Mr. Al Plavel that the adoption of a first coating consisting essen-

tially of titanium nitride provides improvements in the wear properties of the coated sintered carbide substrates, that such improvements are based upon what is believed to be a reduction in the depletion of carbon at the surface of the sintered carbon substrate during the coating operation when titanium nitride is coated onto the sintered carbide substrate as compared with the depletion of carbon on the sintered carbide substrate when either titanium carbide is coated onto said surface or when an attempt is made to carburize the surface by exposing the sintered carbide substrate at an elevated temperature to a hydrocarbon gas in an effort to increase the carbon content at the surface of the sintered carbide substrate; that the phase of the sintered carbide substrate formed at the surface thereof when carbon is depleted by the coating process steps is referred to in the trade as "eta-phase"; that the production of such a phase during coating processing is considered in this technology as deleterious to the wear properties of the coated carbide substrate;

That it is his opinion based upon statements of Mr. Al Plavel of Ti-Coating, Inc. and the written comments of Dr. John M. Blocher, Jr. in correspondence dated November 13, 1984 addressed to Mr. C. V. Zichichi of Ti-Coating, Inc., that the application of a titanium nitride coating to a sintered carbide substrate decreases the tendency of carbon to be leached out of the substrate during the coating process and therefore the foremation of an eta-phase at the surface of the sintered carbide substrate on the basis that the thermodynamics do not favor the extraction of carbon from the substrate during the application of a titanium nitride coating.

That in discussions with Mr. Al Plavel of Ti-Coating, Inc. he has been advised that the formation of said eta-phase to the extent of merely a five micron thickness can result in as much as 50% loss in strength of the coated sin-

tered carbide substrate, as indicated by the literature in this field;

3. That at the request of Hugh McGuire, Esq., counsel for Ti-Coating, Inc., he has made a study of a process according to Mr. McGuire, adopted as of November 1, 1982 by Ti-Coating, Inc. together with a study of:

(a) U.S. patent 4,101,703 and its file history, Serial No. 571,695 and the file history of a parent application Serial No. 329,128 and references cited therein,

(b) U.S. patent 4,162,388 [*sic*] and its file history Serial No. 875,071 and the references cited therein,

(c) the file history of Interference 99,391, and

(d) the file history of U.S. 3,874,900 to Post et al, Serial No. 387,665;

4. That based upon his study of the process and the documents enumerated in paragraph 3, he has given consideration to the question of infringement of the claims of the '703 patent and the '338 patent by the articles produced by Ti-Coating, Inc. and the process of making same which are described above in paragraph 2 and has arrived at the following opinion:

(a) The scope of all of the claims (1-19) of the '703 patent, considered in view of the references cited in Application Serial No. 571,695 and specifically with respect to W. German patent 1,954,336, U.S. patent 3,684,565, and the remarks made by the applicant during prosecution of the application in light of the principles set forth by the Federal Circuit in *Hughes Aircraft Co.* v. *U.S.*, 219 USPQ 473, 481 (Fed. Cir. 1983) and *Coleco Industries, Inc.* v. *I.T.C.*, 197 USPQ 472, 573, F.2d 1247, 1257 (CCPA 1978) are limited to:

an article, a tool, or a wear part of a tool having:

(1) a substrate which may be a hard metal or sintered carbide;

(2) a composite coating including
   (a) a first layer of a metal carbide, of titanium or other metal listed in claim 8, *directly* on the substrate surface, and
   (b) a top layer overlying the first layer of a metal nitride or, alternatively, an intermediate titanium carbonitride layer between the first layer and the top layer;

(b) The broadest claims of the '703 patent, namely, claims 1, 3, 6, 8, 15, 16, 17, and 19 are not of sufficient scope to encompass the coated metal carbide substrate articles produced by the process of Ti-Coating, Inc.;

(c) The scope of all of the claims (1-24) of the '338 patent, considered in view of the references cited in Application Serial No. 875,071 and Application Serial No. 571,695, and specifically with respect to W. German Patent 1,954,366 when taken either alone or in combination with U.S. Patent 3,684,565 and the remarks made by the applicant during prosecution of the application in light of the principles set forth by the Federal Circuit in *Hughes Aircraft* v. *U.S.*, cited above, and *Coleco Industries, Inc.* v. *I.T.C.*, cited above, are limited to:

a method of producing an article which may be a hard metal or a sintered carbide substrate having a composite coating including:

(1) a first layer of titanium carbide *directly* on the substrate surface and

(2) a top layer overlying the first layer of a titanium nitride, or alternatively, an intermediate titanium carbonitride layer between the first layer and the top layer,

said coatings deposited on said sintered carbide substrate by reacting a gaseous mixture of a titan-

ium halide, a hydrocarbon gas, and hydrogen to form the first layer of titanium carbide and thereafter reacting the titanium carbide coated sintered carbide substrate with a gaseous mixture containing a titanium halide, a nitrogen-containing gas, and hydrogen to form a top layer of titanium nitride or, alternatively, forming an intermediate titanium carbonitride layer between the first layer and the top layer, by reacting a gaseous mixture of a titanium halide, a hydrocarbon gas, a nitrogen-containing gas, and hydrogen.

(d) The broadest claims of the '338 patent, namely, claims 1, 2, 3, 20, and 16, are not of sufficient scope to encompass the process of producing sintered carbide substrates coated with the wear-resistant layers of Ti-Coating, Inc.

It is therefore his opinion that the use by Ti-Coating, Inc. of the process described above to form articles, or tools does not infringe any of the claims of the '388 [*sic*] patent or any of the claims of the '703 patent.

5. That if called upon to testify in this matter, he is competent to testify and will testify as outlined above.

FURTHER, Affiant sayeth not.

/s/ Andrew E. Pierce

(*Jurat Omitted*)

APPENDIX K

LETTER FROM DR. JOHN M. BLOCHER, JR.

DR. JOHN M. BLOCHER, JR.
CONSULTANT

915 Silvoor Lane
Oxford, Ohio 45056, U. S. A.
(513) 523-2311

Mr. C. V. Zichichi
Ti-Coating, Inc.
42123 Irwin
Mt. Clemens, MI 48045

13 November, 1984

Dear Mr. Zichichi,

Thank you for your interest in having me review the Schintelmeister [*sic*] patents as they relate to your production of TiN/TiC/TiN coatings. I hope that my analysis will be of value to you.

I will comment first on the technical aspects of your applying a base coating of TiN adjacent the substrate and below the TiC/TiN coating cited in the patents, and then take up the question of how the patents relate to that combination.

Your argument that the application of a base coating of TiN decreases the tendency to leach carbon from the substrate and form eta-phase material is basically sound. The reaction

$$C + TiN = TiC + N_2 \qquad (1)$$

must occur to extract carbon from the substrate and introduce it into a TiN coating covering the substrate. This reaction can occur only with the driving force of a negative free-energy change. Below are tabulated the free-energy changes calculated for the reaction over the temperature range of interest (thermodynamic data from the JANAF Tables).

Temperature, K	*Free Energy Change, kcal/mol*
1000	(+) 16.039
1100	14.102
1200	12.179
1300	10.258
1400	8.374

As you can see, the free-energy change is positive in all cases, indicating that the reaction will not be favored as written. However, some qualification is in order.

Equation (1) assumes that the nitrogen is rejected into an atmosphere containing nitrogen at the standard condition, 1 atm. For example, at 1400K carbon would tend to react with TiN at nitrogen partial pressures below 0.05 atm. At 1000K the equilibrium N_2 pressure would be 0.0003 atm. This must be taken into consideration in your processing. Further, the TiN must be the nitrogen-saturated phase. As you know, the homogeneity range for TiN (as well as TiC) is extensive, and any titanium in excess of the saturation limit would tend to leach carbon from the base. I do not have the data at hand necessary to treat this question quantitatively. However, you should strive for a nitrogen-saturated TiN phase.

Even though the partial pressure of nitrogen should fall below the above equilibrium values, for example while a TiC coating were being applied in a nitrogen-free atmosphere, the reaction represented by Equation (1) would be limited by the rate at which nitrogen (and carbon) could diffuse through the TiN coating. Again, I do not have the data at hand to make a quantitative prediction. However, my hunch is that at 1300K, for example, the diffusion rate is slow enough to be in your favor. You probably have the data to support the suppression of eta-phase formation by your use of a TiN intermediate, which would be more convincing that [*sic*] the diffusion calculations anyway.

It should be noted that Equation (1) assumes that the carbon in the base is present at unit activity, i.e., it is present as pure graphite. Actually, it is in solution in the substrate at reduced activity, thus further decreasing the tendency of Equation (1) to move to the right. The fact that the solid solution TiCN is actually being formed in the displacement of nitrogen will modify the real free-energy changes in Equation 1. Again, I do not have the data at hand to assess this factor. However, the direction will always be toward nitridation of the carbide rather than carburization of the nitride.

Now, to take up the question of patent coverage. In order to clarify the picture, I tabulated the features of the pertinent claims of the two patents, one of which U.S. 4,101,703 is a product patent and 4,162,338 is a process patent for that product, with the exception that the latter is limited to titanium carbide and nitride coatings, whereas the former claims a host of other carbides and nitrides.

This tabulation includes the claim number, substrate identification, whether or not the substrate is directed to be precarburized, whether or not the carbide coating is stipulated to be adjacent the substrate, whether the overall coating "comprises" (C) TiC and TiN or "includes" (I) TiC and TiN (this may become important), the nature of the coatings, and the nature of the coating reactants.

(Tabulation appears on following page)

4,101,703

Claim	*Subs.*	*Carb.?*	*Adj.?*	*C/I*	*C1*	*C2*	*C3*	*R1*	*R2*	*R3*
1	HM,SC	Y	Y	C	TiC	TiN	–	TiX (C,H)	TiX (N,H)	–
2	CC	..	..	..	..	..	..	..	..	..
3	HM,SC	-	-	I	TiC	TiN	–	–	–	–
5	CC	..	..	..	..	..	..	..	..	..
6	HM,SC	-	Y	Y	TiC	TiN	–	–	–	–
7	CC	..	..	..	..	..	..	..	..	..
8	CC	-	Y	C	MC	MN	–	–	–	–
15	HM,SC	-	-	I	TiC	TiCN	TiN	–	–	–
16	HM,SC	-	Y	C	TiC	TiCN	TiN	–	–	–
17	CC	-	Y	C	MC	MCN	MN	–	–	–

4,162,338

1	HM,CC	-	Y	C	TiC	TiN	–	TiX (C,H)	TiX (N,H)	–
2	HM,CC	-	Y	C	TiC	TiCN	TiN	TiX (C,H)	TiX (CHN)	TiX (C,H)
3	CC	-	Y	C	TiC	TiCN	TiN	TiX (C,H)	TiX (CHN)	TiX (C,H)

4 (Ditto 3, deposition at subatmospheric pressures)
5 (Ditto 3, addition of inert gases)
6 (Ditto 3, substrate surface carburized)
7 (Ditto 1, substrate surface carburized)
8 (Ditto 2, substrate surface carburized)

16	CC	-	Y	C	TiC	TiN	–	TiX (C,H)	TiX (C,N)	–

17 (Ditto 16, TiX = $TiCl_4$, (C) = methane (N) = nitrogen)
18 (Ditto 17, gas contains also Hydrogen and argon)
20 (Ditto 16, intermediate TiCN coating)
24 (Ditto 17, gas at subatmospheric pressure)

Key:

Col. 2: HM = hard metal, SC,CC = sintered, cemented carbide
Col. 3: Y = yes, carburization specified

Col. 4: Y = yes, carbide layer adacent substrate
Col. 5: C = comprises (interpreted to mean exclusively)
I = includes (interpreted to imply "among others")
Col. 6-8: MC, MCN, MN = metal carbides, carbonitrides, nitrides
Col. 9-11: TiX = titanium halide;
(C), (N), (H) = carbon-, nitrogen-, hydrogen- containing gases

It will be noted that most of the claims clearly specify that the carbide coating be applied directly to the metal carbide substrate, this to be overcoated with the nitride, with or without an intermediate carbonitride. I am convinced that Schintelmeister either did not anticipate the advantage of using a preliminary nitride coating, or that he avoided its mention for some unexplained reason. Otherwise he would have included a claim that spelled it out. I am, however, disturbed by the wording of Claims 3 and 15 of the product patent, which by use of the word "include" rather than "comprise", might be interpreted to cover the situation in which an intermediate coating is present between the substrate and the first carbide coating. If that is ruled to be the valid interpretation, I would conclude that Schintelmeister "lucked out" on that one, because his intent is obviously not to clearly claim such an intermediate coating. It is to be noted that all of the examples have a carbide coating adjacent the substrate, and that at no place in the text is the possibility of an intervening coating suggested or allowed. It all comes down to the use of the word "include" in Claims 3 and 15.

It was my impression that the most general claims of a patent should come first. The position of claims 3 and 17 in 4,101,703 violate that norm. I'll leave it up to the lawyers to interpret the significance.

Further, I see nothing "surprising" or "unpredictable" in the results that Schintelmeister got from using a composite coating to replace either of the two components. The

result is merely additive by the rationale given in Column 5, Lines 65ff. of the first patent.

With reference to my expertise, I have enclosed a summary of my past experience which includes many references to papers written and patents granted. Those most pertinent to your problem are checked for your attention. Someday I will type the whole thing into my computer so that I can weed out the garbage for a purpose such as yours.

I have enjoyed considering this problem and wish you success in its solution. If I can be of further service to you, let me know. My invoice will follow.

I hope to have the pleasure of seeing you in person some day.

Best wishes.

Sincerely yours,

/s/ John M. Blocher, Jr.

RESUMÉ

Name

John M. Blocher, Jr.

Address

Present: 915 Silvoor Lane, Oxford, Ohio 45056
(513) 523-2311

Latest full-time Employment

Senior Research Scientist, Battelle, Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201, (616) 424-7460 (direct line)

Citizenship/Marital Status

U.S.
Married, 5 children

Objective

Retirement with time to pursue personal interests, but with sufficient involvement in professional interests as a consultant to remain active.

Personal History

Born January 6, 1919, Baltimore, Maryland. Father, Dr. John M. Blocher, Chemistry Professor, Baldwin-Wallace College, Berea, OH; Mother, Sallie Garland Blocher. One sister, Mrs. S. B. Stokes. Attended Berea public schools, Baldwin-Wallace College and the Ohio State University. Married Phyllis Burke 1941; five children, Dr. John David Blocher, Mrs. Joann B. Alexander, Mrs. Kathryn B. McGrew, Mary Sue Blocher, and Richard Burke Blocher.

Personal Interests

Music, carpentry and wood working, natural resources, swimming, ice skating, cycling, German literature.

Professional Interests

Chemical vapor deposition and related technology, computer calculation of chemical equilibris from free-energy data.

Education

B.S. Baldwin-Wallace College, 1940
Major in Chemistry, minors in Math and Physics

PhD. Ohio State University, 1946
Physical Chemistry

Professional Experience

1946-1981	Battelle, Columbus Laboratories
1973-1981	Senior Research Scientist
1969-1973	Fellow, Materials Technology Department
1959-1969	Division Chief
1950-1959	Assistant Division Chief

1946-1950	Research Engineer
[*1984,**] 1981, 1975, 1973, 1970	Co-Editor, Proceedings of the [*Ninth,*] Eighth, Fifth, Fourth and Second Conferences on Chemical Vapor Deposition, The Electrochemical Society, Princeton, New Jersey (1981) (1975, 1973, 1970 resp.)
1966	Co-editor "Vapor Deposition", John Wiley and Sons, New York, 1966, Author of two chapters
1965-1966	Member, Ceramics Processing Panel, President's Materials Advisory Board
1956-1975	Divisional Editor for Electrothermics and Metallurgy, Journal of the Electrochemical Society
1948	Ohio State University, night-school quiz class and lab instructor, chemistry
1944-1945	Tennessee Eastman Corporation, Oak Ridge, Tennessee, Mass spectrometric analysis of uranium isotope concentrates
1943-1944	Capital University, Columbus, Ohio, part-time instructor in physics
1940-1942	Ohio State University, part-time quiz-class instructor, freshman chemistry

Extra-Professional Experience

Choir Director, King Avenue Methodist Church, 7 years
Chairman, Board of Trustees, Wesley Foundation of the Ohio State University, 8 years; treasurer, 5 years
Assistant Scoutmaster and Scoutmaster, Troop 28, Columbus, Ohio, 10 years
Red Cross Water Safety Instructor, active 1958-1967

Professional Society Activities

American Chemical Society
Member, 1940-1965

---

* *Printer's note:* Bracketed insertions indicate handwritten addenda.

Electromechanical Society
Member, 1942-present
Candidate for Vice President,
1980[, *1984 (election pending)*]
Member, Board of Directors, 1977-1979
Chairman Electrothermics and Metallurgy Division, 1977-1979
Executive Committee, E&M Division, 1960-1981
Member, Ways and Means Committee, 1979-1981
Member, Honors and Awards Committee, 1975-1977
Chairman, Becket Award Committee, 1975-1977
Chairman, Organizing Committee C. Wagner Award, 1978-1979
Divisional Editor, Journal of E.C.S., 1956-1975
Organizer, International Conference on Chemical Vapor Deposition (1967-present); Co-chairman and Proceedings Editor, Second, Fourth, Fifth and Eighth (Paris, 1981), Co-Chairman[, *Editor*] Ninth (Cincinnati, OH, 1984)

Sigma Xi
Member, 1946-present

Publications

J. M. Blocher, Jr., and I. E. Campbell, "Carbide Coatings for Graphite", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy", (1958).

J. M. Blocher, Jr., "Chemical Vapor Deposition — A 1973 Perspective", Proceedings of the Fourth International Conference on Chemical Vapor Deposition, October 7-12, 1973, Boston, Massachusetts, The Electrochemical Society, Inc., Princeton, New Jersey, (1973).

J. M. Blocher, Jr., "Some Reflections on the Work of J. H. DeBoer, A. E. Van Arkel, and J. D. Fast; Kinetics of Iodide Chromium Deposition" Proc. 4th Euro

CVD Conf., J. Bloem et al, Eds., Eindhoven 1983, Philips Centre for Manufacturing Technology, 1983.

John M. Blocher, Jr., and J. H. Oxley, "Chemical Vapor Deposition Opens New Horizons in Ceramic Technology", Amer. Ceram. Soc. Bull., 41 (2), 81-84 (Feb. 15, 1962).

J. H. Oxley, M. F. Browning, J. M. Blocher, Jr., and C. E. Dryden, "Coating Costs for Ceramic-Coated Nuclear-Fuel Particles", Nucl. Sci. and Engr., *16* (3), 280-290 (July, 1963).

J. H. Oxley, J. F. Hannah, J. M. Blocher, Jr., "Coating Uranium Dioxide Powders With Metallic Tungsten", Ind. & Engr. Chem., *51*, 1391-1394 (Nov. 1959).

W. H. Pfeifer, W. J. Wilson, N. M. Griesenauer, M. F. Browning, and J. M. Blocher, Jr., "Consolidation of Composite Structures by CVD", Proceedings of the Second International Conference on Chemical Vapor Deposition, May 10-15, 1970, Los Angeles, California, The Electrochemical Society, Inc., Princeton, New Jersey.

J. M. Blocher, Jr., R. F. Ralsten, and I. E. Campbell, "Density and Viscosity of Titanium Tetrabromide", J. Electrochem. Soc., *104*, (9), 553-555 (Sept. 1957).

J. H. Oxley, E. A. Beidler, J. M. Blocher, Jr., C. J. Lyons, R. S. Park, and J. H. Pearson, "Fluidized-Bed Process for Production of Tungsten", Nucl. Appl., *1*, 567-574 (Dec. 1965).

J. M. Blocher, Jr., M. F. Browning, and J. H. Oxley, "Fluidized-Bed Processing of Particulate Nuclear Fuels", Nucl. Eng., Part XV, Chemical Engineering Progress Symposium Series, *62*, (65), 64-78, Am. Inst. Chem. Engrs., New York (1966).

J. H. Oxley, E. A. Beidler, J. M. Blocher, Jr., C. J. Lyons, R. S. Park, and J. H. Pearson, "Fluoride Tungsten", 1964 Plansee Proceedings (1965), p. 278-300.

J. H. Oxley, E. A. Beidler, J. M. Blocher, Jr., C. J. Lyons, R. S. Park, and J. H. Pearson, "Fluoride Tungsten", Am. Nucl. Soc. Trans., *7* (2), 426 (Nov. 1964).

J. M. Blocher, Jr., "Forming Parts from Vapors", Machine Design, June 24, 1971.

E. H. Hall and J. M. Blocher, Jr., "Heat of Formation of Titanium Tribromide by the Mercury Reduction of Titanium Tetrabromide", J. Electrochem. Soc., *105* (1), 40-43 (Jan. 1958).

J. M. Blocher, Jr., "Incremental Gas-Phase Molecular Transport", Chap. 3, *Ceramic Processing*, Materials Advisory Board, Publication No. 1576, National Academy of Sciences, Washington, D.C., 1968, pp. 84-105.

T. Gabor and J. M. Blocher, Jr., "In Situ Electronmicroscopic Study of the Growth of Iron Whiskers by Chemical Vapor Deposition", J. Appl. Phys., *40*, (7), 2696-2704 (June, 1969).

J. M. Blocher, Jr., "Integrating Factors in Chemical Vapor Deposition", Proceedings of the Conference on Chemical Vapor Deposition of Refractory Metals, Alloys, and Compounds, Amer. Nucl. Soc., Hinsdale, Ill. (1967).

J. H. Oxley, A. C. Secrest, N. D. Veigel, and J. M. Blocher, Jr., "Kinetics of Carbon Deposition in a Fluidized Bed", A. I. Ch. E. Journal, *7*, (3), 498-501 (Sept. 1961).

H. E. Carlton, J. H. Oxley, E. H. Hall, and J. M. Blocher, Jr., "Kinetics of the Hydrogen Reduction of Boron Trichloride to Boron", Proceedings of the Second International Conference on Chemical Vapor Deposition, Los Angeles, California, May 10-15, 1970, p. 209, The Electrochemical Society, Inc., Princeton, New Jersey (1970).

J. H. Oxley and J. M. Blocher, Jr., "Mass and Heat Transfer During the Chemical Vapor Deposition of

Metals", J. Eectrochem. Soc., *108* (5), 460-464 (May 1961).

J. H. Oxley, M. F. Browning, N. D. Veigel, and J. M. Blocher, Jr., "Microminiaturized Fuel Elements by Vapor-Deposition Techniques", I&EC; Product Research and Development, *1* (2), 102-107 (June 1962).

J. M. Blocher, Jr., "Nitrides", Chap. 11 from *High-Temperature Materials and Technology*, I. E. Campbell and E. M. Sherwood, Ed., John Wiley & Sons, Inc., New York (1967), p. 379-398.

T. Gabor and J. M. Blocher, Jr., "Non-equilibrium Chemical Reactivity of Polycrystalline Iron Foils", J. Vac. Sci. & Tech., *6* (1), 73-78 (1969).

J. M. Blocher, Jr. and A. B. Garrett, "The Photovoltaic Effect. The Spectral Sensitivities of Cadmium, Zinc, and Silver Electrodes: the Effect of pH and Oxygen", J. Am. Chem. Soc., *69*, 1594 (1947).

J. M. Blocher, Jr., "Plating by Reaction of Gaseous Compounds", Proceedings of "Surface 66", Int. Conf. on Protection Against Corrosion by Metal Finishing, Basel, Switzerland, Nov. 23, 1966, p. 133-141.

M. F. Browning, A. C. Secrest, V. M. Secrest, R. B. Landrigan, and J. M. Blocher, Jr., "Preparation and Evaluation of Carbon-Coated Fuel Particles", in "Preparation and Processing of Particulate Nuclear Fuels", USAEC Rpt. CONF-117.

W. J. Wilson, M. T. Browning, and J. M. Blocher, Jr., "The Preparation and Properties of BeO-Coated UO_2 Particles", published version appears as "Oxide Coating Studies", USAEC Rept. BMI-1600 (Del.), pp L1-L7, Nov. 1, 1962.

I. E. Campbell, R. I. Jaffee, J. M. Blocher, Jr., J. Gurland, and B. W. Gonser, "Preparation and Properties of Pure Titanium", J. Electrochem. Soc., 93 (6), 271-285 (June, 1948).

N. D. Veigel, J. M. Blocher, Jr., and M. F. Browning, "Preparation and Properties of Thoriated Chromium", Proceedings of Third International Conference on Chemical Vapor Deposition, Salt Lake City, Utah, April 24-27, 1972, p. 200-213, American Nuclear Society, Hinsdale, Illinois (1972).

C. F. Powell, C. H. Ish, and J. M. Blocher, Jr., "The Preparation of High-Purity Boron by Hot-Wire Techniques", *Boron Synthesis, Structure and Properties*, Plenum Press, Inc., New York (1960), 7-14.

J. M. Blocher, Jr., M. F. Browning, A. C. Secrest, V. M. Secrest, and J. H. Oxley, "Preparation of Ceramic-Coated Nuclear-Fuel Particles", Nuclear Reactor Chemistry, Second Conference Proceedings, Gatlinburg, Tennessee, Oct. 10-12, 1961, TID-7622, p. 57-63.

N. D. Veigel and J. M. Blocher, Jr., "Preparation of Small Samples of Ductile Titanium and Zirconium from the Isotopic Oxides by Iodide Refining", J. Electrochem Soc., *109* (7), 647-648 (July 1962).

J. M. Blocher, Jr., M. F. Browning, W. J. Wilson, V. M. Secrest, A. C. Secrest, R. B. Landrigan, and J. H. Oxley, "Properties of Ceramic-Coated Nuclear-Fuel Particles", Nucl. Sci., & Eng., *20*, 153-170 (1964).

R. J. Runck, T. E. Pearnside, J. M. Blocher, Jr., and I. E. Campbell, "Properties of Iodide Chromium", Paper from Ductile Chromium and Its Alloys, Amer. Soc. Metals, 129-137 (1957).

C. A. Krier and J. M. Blocher, Jr., "Recent Developments in Coatings for Refractory Materials", J. Electrochem. Technol., *1* (5-6), 137-147 (May-June 1963).

J. M. Blocher, Jr., and M. F. Browning, "The Role of Chemical Vapor Deposition in the Production of High-Purity Silicon", Proceedings of the Sixth International Conference on Chemical Vapor Deposition,

The Electrochemical Society, Inc., Princeton, New Jersey, 1977.

J. M. Blocher, Jr., "Structure/Property/Process Relationships in Chemical Vapor Deposition", J. Vacuum Science and Technology, *11*, 680-686 (1974).

L. M. Litz and J. M. Blocher, Jr., "Sulfides", *High Temperature Materials and Technology*, John Wiley & Sons, Inc., New York (1967), p. 431-454.

J. M. Blocher, Jr., M. F. Browning, and W. J. Wilson, "Survey of Options in a Balanced System for Production of Silicon by Thermal Decomposition of Trichlorosilane", Proceedings of the Seventh International Conference on Chemical Vapor Deposition, The Electrochemical Society, Inc., Princeton, New Jersey, 1979.

E. H. Hall and J. M. Blocher, Jr., "Thermodynamics of the Disproportionation of Titanium Tribromide", J. Phys. Chem., *63*, 1525-1526 (Sept. 1959).

J. M. Blocher, Jr., and E. H. Hall, "Thermodynamics of the Mercury Reduction of Titanium Tetrafluoride", J. Phys. Chem., *63*, 127-128 (Jan. 1958).

C. F. Powell, J. H. Oxley and J. M. Blocher, Jr., *Vapor Deposition*, John Wiley & Sons, Inc., New York (1966), 725 pp.

W. J. Wilson, M. F. Browning, and J. M. Blocher, Jr., "Vapor Deposition of Wear-Resistant Coatings", Proceedings of the Twenty-Third Meeting of the Mechanical Failures Prevention Group, 1975, U.S. National Bureau of Standards Special Publication V-452, 1976, pp. 151-169.

E. M. Sherwood, D. M. Rosenbaum, J. M. Blocher, Jr., and I. E. Campbell, "The Vapor Pressure of Rhenium", J. Electrochem. Soc., *102*, 650-654 (Nov. 1955).

John M. Blocher, Jr. and I. E. Campbell, "Vapor Pressure of Titanium", J. Am. Chem. Soc. *71*, 4040 (1949).

E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, "Vapor Pressure of Titanium Tetrabromide", J. Electrochem. Soc., 105, 271-275 (May 1978).

E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, "Vapor Pressure of Titanium Tetrafluoride", J. Electrochem. Soc., *105*, 275-378 (May 1958).

Patents

(Two high-purity silicon process patents, assigned to Texas Instruments, Inc., record not available 10, Nov., 1983)

J. M. Blocher, Jr., M. F. Browning, and R. W. Dayton, "Coated Nuclear Reactor Fuel Particle of UO_2 and Method of Making the Same", U.S. Patent 3,290,223 (Dec. 6, 1966). Assigned to U.S. Atomic Energy Commission.

L. D. Stoughton, J. M. Blocher, Jr., and N. D. Veigel, "Ceramic-Coated Fuel Particles", U. S. Patent 3,121,047 (Feb. 11, 1964). Assigned to the U. S. Atomic Energy Commission.

L. D. Stoughton, J. M. Blocher, Jr., and N. D. Veigel, "Ceramic-Coated Fuel Particles", U. S. Patent 3,165,422 (Jan. 12, 1965). Assigned to the U. S. Atomic Energy Commission.

J. H. Oxley, C. F. Powell, and J. M. Blocher, Jr., "Chemical Vapor Plating Process", U.S. Patent 3,178,308. Assigned to Pfaudler Permutit, Inc.

I. E. Campbell and J. M. Blocher, Jr., "Dissociation-Deposition Unit for the Production of Chromium", U.S. Patent 2,955,566 (Oct. 11, 1960). Assigned to Chilean Nitrate Sales Corp.

J. M. Blocher, Jr., "Flow Seal Systems", U.S. Patent 3,118,727 (Jan. 21, 1964). Assigned to United States of America as represented by the Secretary of the Navy.

J. M. Blocher, Jr.and M. F. Browning, "Method for Coating Actinide Particles", U.S. Patent 3,175,922 (March

30, 1965). Assigned to the U.S. Atomic Energy Commission.

J. M. Blocher, Jr., "Nuclear Fuel Particles Coated with Mixture of Pyrolytic Carbon and Silicon Carbide", U.S. Patent 3,249,509 (May 3, 1966). Assigned to the U.S. Atomic Energy Commission.

J. M. Blocher, Jr. and A. C. Loonam, "Process and Apparatus for the Production of Metallic Chromium", Can. Patent 592,216 (Feb. 9, 1960). Assigned to Chilean Nitrate Sales Corp.

J. M. Blocher, Jr., and M. F. Browning, "Process for Silicon and Trichlorosilane Production", U.S. Patent 4,117,094 (Sept. 26, 1978). Assigned to Texas Instruments, Inc.

J. M. Blocher, Jr. and A. C. Loonam, "Production of Metallic Chromium", Can. Patent 620,235 (May 16, 1961). Assigned to Chilean Nitrate Sales Corp.

J. H. Oxley and J. M. Blocher, Jr., "Production of Rigid Shapes of Refractory Metals by Decomposition of the Metal Hexafluoride in the Intertices of a Green Compact", U. S. Patent 3,373,018 (Mar. 12, 1968). Assigned to Allied Chemical Corporation.

J. M. Blocher, Jr. and J. H. Pearson, "Reduction of Tungsten Hexafluoride to Form Improved Tungsten Particles", U. S. Patent 3,234,007 (Feb. 8, 1966). Assigned to Allied Chemical Corporation.

J. M. Blocher, Jr., "Refractory Metal Structures and Their Preparation", Can. Pat. 837,002 (Mar. 17, 1970). Assigned to Allied Chemical Corporation.

J. M. Blocher, Jr., M. D. Veigel, and R. B. Landrigan, "Vapor Deposition of Hardened Niobium", U.S. Pat. 4,380,556 (Apr. 19, 1983). Assigned to the U.S. Department of Energy.

(others pending)

Talks and Presentations

Numerous, not conveniently documented. Listed below are invited presentations scheduled for 1980:

"Current Trends in Chemical Vapor Deposition", WESTECH-80 Conference, Los Angeles, California, March 17-20.

"Chemical Vapor Deposition of Ceramic Materials", American Ceramic Society Meeting, Chicago, Illinois, April 27-30.

"Chemical Vapor Deposition", UCLA Short Course on Deposition Technologies and Applications (presented also in 1978, 1979), Los Angeles, California, June 16-20.

"Coating of Glass by Chemical Vapor Deposition", Seminar on Glass Coatings, Geneva, Switzerland, September 17-19.

"Developments in the Technology of Chemical Vapor Deposition", Tenth World Conference on Metal Finishing, Kyoto, Japan, October 12-17.

APPENDIX L

SCHINTLMEISTER'S REPLY IN SUPPORT OF ITS MOTION TO DISMISS OHLSSON'S RULE 231(a)(1) MOTION

(United States Patent and Trademark Office — Before the Board of Patent Interferences)

(Dated February 4, 1977)

(ROBERT C. POST, et al, v. FALL J. O. W. OHLSSON, et al, v. WILFRIED SCHINTLMEISTER — Interference No. 99,391)

Junior party Ohlsson et al has now clearly shown its violation of the rules and practice in bringing a motion to dissolve the interference on grounds of unpatentability both to itself and to senior party Schintlmeister. Ohlsson has done so by now specifically indicating that it believes the invention unpatentable to patentee Post as well.

Ohlsson's present comments are directly contrary to the comments Ohlsson made during its own *ex parte* prosecution. It is clear that the only reason Ohlsson brought the motion was fear of having priority awarded against it. Ohlsson, in its Preliminary Statement, alleges entitlement to a Swedish application filed later than the Austrian application, the benefit of which was accorded by the Examiner to Schintlmeister.

The party Ohlsson et al, whose assignee is the Swedish company Sandvik, relies upon some 14 separate references in an effort to show unpatentability. However, at least 11 of those references have been long known to Sandvik, since Sandvik sought to apply those references in an opposition proceeding filed in the United Kingdom against Cutanit, Ltd. British patent No. 1,425,633. A twelfth reference, United States patent No. 3,616,506, is apparently actually owned by Sandvik.

Notwithstanding the prior knowledge by Sandvik of most of the same references it now cites in opposing patentability, Sandvik in this country filed an appeal brief in this very application, lauding the unexpected and unobvious nature of the very invention called for by the interference counts. A copy of the Sandvik appeal brief, Paper No. 16 filed April 26, 1976 in application Serial No. 370,549 is annexed hereto as Exhibit A.

The invention of the counts reduced to its fundamentals is the application of a titanium carbide layer over a substrate followed by an overlayer of titanium nitride. In its brief, Exhibit A, the party Ohlsson and their assignee Sandvik were speaking of the same concept. See, e.g., page 3:

> ". . . it was learned that the useful life of the hard metal body could be prolonged by covering the surface of the body with a wear-resisting coating layer of a metallic carbide (e.g., TiC) deposited from gaseous phase.
>
> Applicants discovered that still further advantage can be realized by over-coating the TiC layer with a very thin surface coating layer of TiN (or, TiC·N)."

At page 4 Sandvik and its inventors Ohlsson et al advised the Patent Office that the invention results in increasing the service life of a coating insert by about 300 percent and then go on to note that:

> ". . . the unique value of the thin outer layer of TiN (over the TiC-coated hard metal insert) resides in its application to inserts subjected to intermittent cutting, as in milling operations."

Ohlsson et al then went on in their brief to say that the results of this combination are unexpected and beneficial:

"In this way it has been possible to obtain the optimum wear-resistance (produced by the TiC component) in combination with the optimum toughness (produced by the TiN component) and by a certain combination (= optimizing the thicknesses of the two layers) reach unexpected and very beneficial results. When employed in a milling operation, the effective cutting life of a sintered hard metal insert is increased about 500 percent by giving it a TiC intermediate coating layer plus an outer covering layer — 0.5 micron thick — of TiN, whilst the effective cutting life of this insert is increased only about 45 percent by using only the TiC coating layer without the tough covering layer of TiN.

These improved results, in turning and in intermittent cutting, could not possibly have been foretold by the routineer in the art."

All this was said with knowledge of most of the references now cited as rendering the application unpatentable. Obviously, when Sandvik made the statements to the Patent Office in its brief on appeal, Sandvik did not have the fear of losing the interference and being deprived of a patent. It can only be assumed, in view of an applicant's duty of truth and candor to the Patent Office, that the statements as to the beneficiality and uniqueness, statements of fact made in the brief, were in fact believed to be true by the applicants and their assignee, Sandvik.

While the comments in Sandvik's brief should be sufficient to destroy the efficacy of the current Sandvik unpatentability arguments, a brief word on the substance of the references themselves is believed in order.

None of the references describe a substrate coated with titanium carbide with an overlayer thereon of titanium nitride. To the extent that these references disclose use of more than one coating layer, they teach the necessity of having the *nitride* in contact with the base metal. See, for example, British Patent No. 735,297; British Patent No. 762,931; German Patent No. 1,954,366 and U. S. Patent No. 3,656,995. Indeed, the latter patent explains the art [*sic*] felt need for initially forming a protective nitride barrier layer on the substrate before any further activity.

The other references merely show that the formation of titanium nitride or titanium carbide is known. Yet, each of the applications involved in the interference concedes that much.

None of the references shows the use of a cemented carbide base overlayed with either a nitride or a carbide. Cemented carbide base improvement is, of course, the essential objective of the Schintlmeister invention. The interference counts define a specific relationship of titanium carbide overlaid with titanium nitride and that is simply not disclosed anywhere in any of the references. There is clearly, therefore, no anticipation under 35 U.S.C. § 102. The Patent Office should accept for purposes of this motion the *ante litem motam* assertions of Sandvik as to the technical benefits of the invention. And that being the case, there is certainly nothing within the art recognizing the unique nature of this invention.

Reviewing several of the other references, the Metal Working Production article simply shows that titanium carbide coatings are known and titanium nitride coatings are known, yet there is no indication of a composite coating having a titanium nitride overlayer. British Patent No. 785,236 at page 3, shows a mixed coating, i.e., in which the gaseous mixture in the reaction zone contains

both carbide and nitride forming ingredients thus leading to the formation of a mixed nitride-carbide coating usually referred to as carbonitride and therefore not having the outer layer rich in titanium nitride combined with an inner layer rich in titanium carbide.

Swiss Patent No. 507,094 does not appear to have any relationship to applying titanium carbides or nitrides. It merely describes the use of one or more layers of carbide, nitride, boride or silicide, with no specificity sufficient to anticipate or render the counts obvious under § 103.

U.S. Patent No. 3,616,506 refers to applying a carbide layer on a base with the possible inclusion of some small quantity of oxygen or nitrogen dispersed therein, presumably uniformly and throughout the carbide layer (column 3, lines 45-54). But, this does not have the two different layers called for by the interference counts.

U.S. Patent No. 2,972,556 does not actually relate to the same problem as the problem solved by the interfering applications and patent. The concept of the invention as defined most precisely in Count 3 is improving the wear surface of the tool, i.e., improving its abrasion resistance in use. This presupposes that there be a tool base which is overlaid first with titanium carbide and then titanium nitride. The Schintlmeister application makes clear that there is specific benefit and desirability in the use of a cemented carbide as the base.

U.S. Patent No. 2,972,556 relates to carbon and graphite articles and improving the ability of missile and rocket nose cones made of carbon and graphite to withstand high temperature oxidizing gases flowing past it. But, even then, the procedure of the '556 patent does not involve first a carbide coating followed by a nitride coating. Instead, as pointed out more specifically at column 2, lines 5-30, a metal, which can be any metal which forms a

refractory nitride or carbide, is vaporized and allowed to in part react with the surface of the carbon to form carbide and in part to remain unreacted but merely deposited on the carbon surface. As a next step, nitrogen is introduced and the nitrogen does not form an overlay on the carbide but rather reacts with the deposited metal presumably to form nitrides. At best, therefore, in the process of the '556 patent there would be an overlayer having some carbide and some nitride but there is no provision present for the nitride to be overlying and adjacent the layer of carbide as required by the interference counts.

It is not understood why French Patent No. 2,047,187 was cited in view of its purportedly being based on the same U.S. application as the Reedy patent, No. 3,656,995.

French Patent No. 2,069,774 was provided without a translation and is therefore presumed not pertinent in view of Ohlsson's failure to say anything about it in its papers.

Finally, German Patent No. 1,247,671 refers to having a decarbonized-nitrided surface zone. It is not believed that this has any relationship to the invention here at issue either.

British Patent No. 820,281 likewise does not appear to relate at all to the dual coatings of the interference counts.

CONCLUSION

As we have already pointed out, the motion to dissolve by Ohlsson is improper under the rules. We have also shown that the references are not applicable. Moreover, we have shown the inapplicability out of the very mouth of the same party, i.e., Ohlsson et al, who is now raising the issue of unpatentability. The Rule 231 motion by Ohlsson must be dismissed. Moreover, there is no reason for the Examiner to reconsider patentability in light of the

references raised by Ohlsson. The interference should be allowed to proceed in the normal course. Under the facts of record, that should result in the issuance of an order to show cause why judgment should not be granted in favor of Schintlmeister, the Preliminary Statements of the two junior parties not having alleged dates earlier than the Austrian filing date, the benefit of which has been given to Schintlmeister by the Examiner, and not opposed by any other party.

Respectfully submitted,

/s/ David H. Pfeffer, Reg. No. 19,825
Morgan, Finnegan, Pine, Foley & Lee
Attorneys for the party Schintlmeister
345 Park Avenue
New York, New York 10022
Telephone: 212-758-4800

Dated: February 4, 1977

CERTIFICATE OF SERVICE

I hereby certify that a copy of the foregoing Schintlmeister's Reply In Support Of Its Motion To Dismiss Ohlsson's Rule 231(a)(1) Motion was served by mail, postage prepaid, this 4th day of February, 1977, on each of Jack A. Kanz, Esq., attorney for Post et al at his address of record and upon Ralph E. Parker, Esq., attorney for Ohlsson et al at his address of record.

/s/ David H. Pfeffer

APPENDIX M

AMENDMENT TO UNITED STATES SERIAL NO. 329,128

(In the United States Patent Office)

(Dated August 20, 1974)

Applicant: Wilfried Schintlmeister
Serial No.: 329,128 Group Art Unit 223
Filed: February 2, 1973 Examiner: R. E. Schafer
For: COATED CEMENTED CARBIDE ELEMENTS AND THEIR MANUFACTURE

Hon. Commissioner of Patents August 20, 1974
Washington, D.C. 20231

A M E N D M E N T

S I R:

This is in response to the Official Action dated May 20, 1974.

Please amend the above-identified application as follows:

IN THE CLAIMS:

Please cancel claims 1 and 2 in their entirety.

Please amend claims 3, 7, 8 and 16 according to the provisions of Rule 121(b) by deleting the bracketed [ ] subject matter and inserting the underlined material.

3. (Amended) A cemented carbide substrate bearing an adherent wear-resistant multilayer coating of non-uniform composition varying from layer to layer [in adjoining layers] and wherein said coating contains at least two different wear-resistant materials and includes carbon and nitrogen in chamical combinations with titanium.

7. (Amended) An article according to claim 21 [1] in which an intermediate stratified transition zone is located between parallel underlying and overlying layers of wear-resistant materials of different composition, and the non-uniform composition of material in the strata of said zone gradually differs through the thickness of said zone from a composition approximating that of the underlying layer in the zone stratum adjoining said underlying layer to a composition approximating that of said overlying layer in the zone stratum adjacent to said overlying layer.

8. (Amended) An article according to claim 7 [6] in which the [a] transition zone has a thickness between about 0.1 and 10 microns.

16. (Amended) A method of producing an article according to claim 21 [2] by depositing said adherent coating materials in a plurality of layers of nonuniform composition from reactive gaseous compounds onto said hard sintered base wherein the composition of material in each deposited layer is controlled by controlling the reaction conditions in that deposition stage, including the composition of the mixture of reactive gaseous compounds.

Please add the following new claims 21 and 22.

21. A hard sintered carbide base bearing an adherent multilayer coating of at least two different wear-resistant materials, the composition of said coating varying through its depth or thickness, and said coating comprising at least two elements from the group consisting of carbon, nitrogen, boron, and silicon in chemical combinations with a metal selected from Group III, IV, V and VI of the Periodic Table of Elements having an atomic number of from 21 to 74 and from boron and silicon.

22. The article according to claim 21 wherein the metal component of the coating comprises a mixture of titanium and one or more of said metals.

REMARKS

Claims 3-22 are now presented in this case.

Pursuant to Rule 143, applicant confirms the provisional election of Group I made during the telephone conference referred to in the Official Action of May 20, 1974. Applicant reiterates his traversal of the restriction requirement and respectfully requests reconsideration of this requirement. Group II, claims 16-20, are directed to the method of coating, or more specifically, of producing the articles defined in the claims of Group I. It is submitted that the instant claims do not define two independent and distinct inventions.

This is not a case where an article or composition may be *used* in various different methods or processes which would accord different classifications and distinctions in the art. The instant case presents simply an article and a process for making that article. Moreover, although the Examiner asserts that the "fields of search are not co-extensive" for the Groups I and II claims, it is noted that references from both Class 117 and Class 29 have been cited in the Official Action. For the foregoing reasons, it is respectfully requested that the restriction requirement be reconsidered and that claims 16-20 be subject to examination on the merits in this case.

Claims 1-15 have been rejected under 35 U.S.C. § 112, first paragraph, for being indefinite in the recital of "non-uniform" with respect to the compositions of the coating. The independent claims now presented, namely, claims 3 and 21, specifically state that the non-uniform nature of the coating's composition varies "through its depth or thickness" or "from layer to layer". The antecedent basis for this terminology may be found at page 7, lines 14-25, of the specification. By this amendment it is believed this

rejection is overcome and its withdrawal is respectfully requested.

Claim 1, which recited a coating, has been cancelled without prejudice, thus overcoming the rejection of said claim under 35 U.S.C. § 112.

Before discussing the various rejections asserting prior art against the instant claims, applicant wishes to review some of the advantages of his invention. The present invention relates to wear-resistant articles which comprise a hard sintered carbide base bearing a resistant coating thereon. Such articles are used, for example, in cutting tools. The substrate or hard sintered carbide base is described at page 2, line 8 through page 3, line 18 and at page 5, lines 7-19. These sintered base materials are "solid and coherent masses made by pressing and sintering a mixture of powders of one or more metallic carbides and a much smaller amount of an iron group metal . . . to serve as a binder metal." (Page 2.) The specification describes the wide use of such materials in structural parts and tools which are subjected to intense wear by high compressive strength, mechanical abrasion, and mechanical stress under intense heat. To summarize in a sentence, the present invention relates to a new type of wear-resistant coating deposited on said sintered base material which improve their service life and improve their ability to withstand severe operating conditions including mechanical wear and abrasion. The invention includes the method of coating said substrates.

The coating itself comprises a series of layers or strata with compositions which vary on the thickness or depth of such coating. The composition of the coating is defined in the claims as comprising a non-metal from the group of carbon, nitrogen, boron and silicon, in chemical combination with one or more metals from Groups III, IV, V and VI of the Periodical Table. The preferred metal is titanium,

while even silicon and boron may be used as the metal component in combination with carbon or nitrogen.

As now presented, claims 21, 22, 7 and 8 are directed to the hard sintered base coated with multilayer compositions from the combination of elements noted above. The other claims now presented are directed to a multilayer coating comprising the preferred wear-resistant materials which comprise carbon and nitrogen in chemical combinations with titanium.

Claims 1, 2 and 7 were rejected under 35 U.S.C. § 102 as anticipated by reference "A", the Reedy patent. These claims now correspond to claims 21, 22, 7 and 8. This rejection is respectfully traversed. The instant claims are directed to a coating over a hard *sintered carbide base* material. As noted, *supra*, these materials are clearly and distinctly defined at page 2 et seq. of the instant specification. The Reedy patent, on the other hand, is directed to a coating for "titanium-containing substates". These substrates are not the hard materials for withstanding the severe operating conditions as required by the claimed substrates. Secondly, the substrates of Reedy are not sintered carbide bases.

The most detailed description of the substrate material in Reedy is set forth at Column 4, lines 38-47.

> "As heretofore pointed out, particular substrates which may be coated according to the process of this invention may be pure titanium or titanium alloys containing substantially any number of metals other than titanium in substantially any proportion. The process is particularly well suited to coating either pure titanium or titanium alloys containing titanium as a major constituent, that is, 80 percent or greater, utilizing a gaseous stream containing titanium tetrachloride, natural gas, hydro-

> gen, and nitrogen under heretofore-noted reaction conditions."

The examples in the patent describe the coating of an alloy of titanium-aluminum-vanadium and pure titanium samples. Moreover, the Examiner recognizes that Reedy does not teach the cemented carbide substrate herein claimed in the rejection under 35 U.S.C. § 103 discussed, *infra*.

The purpose of the coating in Reedy is not to improve the physical wear and compressive strength of the coated article, but apparently to improve its impermeability to various chemicals including oxidation resistance.

> "Accordingly, an object of this invention is to provide a process for applying an adherent, nonporous, oxidation-resistant metal carbide, nitride, or carbonitride coating on a titanium substrate. . . ." Column 5, lines 9-12.

It is further noted, that although the Reedy reference disclosed two layers over the titanium substrate, the first layer is not for wear-resistance but rather forms a barrier layer which is described as being important for protection of the titanium from reacting with the constituents in the coating, and to promote the adhesion of the final coating to the substrate. See Column 2, lines 42-66. For the foregoing reasons it is believed that the Reedy patent does not anticipate claims 21, 22, 7 and 8 and the rejection thereover on these grounds should be withdrawn.

Claims 3-6 and 8-15 have been rejected under 35 U.S.C. § 103 as being obvious over Reedy ("A") in view of Wakefield ("B") and Stroup et al ("C"). The Examiner in his remarks concerning this rejection concedes that the Reedy patent does not relate to the coating of "ceramic substrates":

> "Obvious to apply the technique of A to ceramic substrates, as in A, including cemented carbides, as is C, to obtain the desired products."

Again, the Examiner contends that the Stroup et al patent is the only one that defines a sintered carbide base as the substrate being coated. See Column 1, lines 66-67. The relevance of the Stroup et al patent with the article of the instant claims ends, however, with the substrate. It is true that the Stroup et al coated article is used in tools, and machine parts that require resistance to excessive wear and abrasion. However, Stroup at al only teaches the formation of a titanium carbide layer on the substrate. There is no disclosure of a multiplicity of layers nor layers varying in composition. Therefore, the sum of the Stroup at al disclosure is that sintered carbide substrates may be coated with titanium carbide to improve resistance to wear and abrasion. This is not the invention of the instant claims. The instant claims require at least two *non-metals*, i.e., "at least two elements of the group consisting of carbon, nitrogen, boron and silicon" to be in chemical combination with the titanium. The Stroup at al patent only teaches titanium carbides with an "interlayer" at the surface of the substrate containing some of the metal in the substrate.

There is no teaching to link or bridge the single composition coating of the sintered carbides of Stroup at al to the coating of titanium alloys or pure titanium metals of Reedy. Certainly, the Wakefield patent does not satisfy this deficiency in teaching. The Wakefield patent relates to a coating for substrates such as graphite, ferrous metals, titanium alloys and the like. Column 2, lines 46-48. The coating of Wakefield is a carbonitride of a metal selected from silicon, boron, and the transition metals in Groups IV B, V B and VI B of the Periodic Table. Column 2, lines

58-60. Wakefield, again, teaches a single coating of a uniform composition of a carbonitride.

The instant claims require a multilayer coating of non-uniform composition wherin there is at least two different materials present, i.e., titanium carbide, titanium carbonitride, and titanium nitride. Combining the teachings of Wakefield and Stroup et al, one finds two different substrates treated and two different coatings used to treat the two different substrates. The substitution of the carbonitride coating of Wakefield for the titanium carbide coating of Stroup et al would not be obvious and certainly, the addition of the Wakefield coating onto the already coated article of Stroup et al would not be obvoius. Again, while Reedy may teach more than one layer in its coating, one cannot forget that the Reedy patent uses a different substrate from the sintered carbides of Stroup et al and that the barrier layer of Reedy is not for strengteh or hardness but rather for promotion of adhesion and chemical resistance. There is, therefore, no rationale to combine the teachings.

It is further noted that additional distinctions are clear when one reviews the various dependent claims presented herein. For example, the first layer of Reedy, which is adjacent to the substrate, is a barrier layer which is nitrogen-rich forming a titanium nitride layer. (See Column 2, lines 67-75; Column 6, line 56 and claim 1.) In claims 13 and 14, for example, it is a carbon-rich layer which is in closest contact to the cemented carbide substrate and the nitrogen-rich material is in the outermost or surface layer.

None of the references cited disclose the layer thicknesses recited in claims 9-11.

Also, the Reedy patent, which is the only reference which discloses multiple layers of different compositions,

defines only two layers. The first is a barrier layer formed by nitriding the substrate surface. Preferably, the barrier layer and final coating are titanium nitride. Column 7, lines 11-22. It is noted that Reedy also teaches the coating of titanium carbide over the nitride barrier layer. However, this coating appears to exclude any transition zone as recited in claims 11, 14 and 15 where the nitrogen-rich layer *gradually* varies to the carbon-rich layer. For example, the Reedy process for such coating requires the purging of nitrogen from the coating system before beginning the carbon-rich coating:

> "Thus, the barrier layer may be applied by exposing the substrate to a nitrogen atmosphere at elevated temperatures, the nitrogen may then be purged from the reactant chamber, and the substrate finally contacted with hydrogen, a carbon-containing compound, and a metal of the previously noted group in order to deposit the desired carbide coating." Column 7, lines 39-44.

Therefore, the prior art asserted does not teach or render obvious the invention as defined in claims 11, 14 and 15.

For the reasons set forth above, it is believed the three references asserted against the claims, namely, Reedy, Wakefield and Stroup et al, do not teach or render obvious the claimed invention and the rejection thereover should be withdrawn.

Various other references are cited and made of record by the Examiner but are not relied upon in any rejection. A brief review of these references indicates that they are no more relevant than those discussed above. For example, while at least the "E", "G", "H", "A" and "B" references disclose the coating of cemented carbide substrates, the coating is not of a multilayeer or multiple material composition as defined by the instant claims.

For the foregoing reasons, it is believed this case is now in condition for allowance and the passage of this case to issue is respectfully solicited.

Respectfully submitted,

MORGAN, FINNEGAN, DURHAM & PINE
/s/ Arnold I. Rady
Registration No. 26,601

345 Park Avenue
New York, New York 10022
(212) 758-4800